Chem Ed

EDITORIALLY SPEAKING

The legend of Albert Einstein's failure in his mathematics course is one that teachers never should forget. The disturbing uncertainty is not whether the story is true or apocryphal; it could happen in any of our classes. Before we disdainfully assign the villain's role to the unimaginative lout of a teacher —or with a defensive loyalty to our counterpart in the narrative, decide that the intractable Albert must have been a day-dreaming brat, we should take a good look at what goes on in our own classes. The infinitesimal probability of encountering another Einstein is beside the point. So is the argument that for every near-genius there are dozens of similarly-behaving crackpots. —The vital question that the tale should raise is, "What am I doing to encourage (dare I say *develop?*) creativity in my students?"

Anyone with a little insight can see that much of our conventional science teaching blocks rather than encourages real creativity. The student, especially the brilliant student, is delighted to find a subject in which he can revel in the psychological security of a "correct" answer. He knows when he is right—not merely because the professor or the book says so—but because the wonderful consistency of science gives him confidence in the validity of the answer he has obtained by careful use of an established procedure.

It is true that the science teacher is obliged first of all to instill a discipline. Precision is learned by drill, and analytical thinking by practice with illustrative problems of graded complexity. It is important that the student be given the opportunity to learn as many of the pertinent facts as he possibly can before he begins to manipulate any of them. But if this is the limit of the instructor's role, he becomes an academic drill sergeant who will turn out technicians, not scientists.

The conformity that rules the legendary grey flannel-suited yes-boys of Madison Avenue is mild beside what sometimes passes for science instruction. Witness the spectacle of a class of freshmen (clad, incidentally, in the current fashion-dictated uniform of the school), all solving the same stoichiometry problem by a method which even prescribes where the numbers must be written! Or, near the end of the term, witness the "smooth-running" laboratory where success has rewarded only those who have learned to follow directions.

The argument is not that total abandonment of drill or the chaos of undirected experimentation will make a science course successful. But what our classes often woefully lack is the planned opportunity for imagination to flourish. Academic colleagues in other areas are fortunate in having available a simple device. After the discussion of examples they can assign the composing of a poem, a melody, or a still life. Fostering the same essential human attribute for research—the imagination—is more difficult in the science class. The paradox of training in the discipline of scientific methodology and exercising the mind so trained in true exploration need not attain an "either-or" status. It can be resolved, at least partially, by the instructor who recognizes it and attacks the problem with ingenuity.

Good teaching varies its specific devices both with individuals and with subject matter. However, conscientious planning should insure giving every student the chance to act like a scientist. Problems illustrating learned procedures should be followed by ones for which known answers can be reached by a variety of methods. These, in turn, can be followed by problems for which answers are known but methods must be devised. Finally every course should reach its climax in the problems for which neither answers nor methods are known—problems which the student realizes are not mere confirmations of what hundreds of his predecessors have already established.

We should not indulge either in disdainful castigation or overabundant sympathy for that mathematics teacher who never touched the life of Einstein. Rather, we should make sure that history does not repeat itself.

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Science, Literature, and Human Thought

As I have mentioned elsewhere,[1] that morning star of modern chemistry, Joseph Black, in the words of Lord Brougham, "liked to dwell on the manner in which discoveries are made, and the practical effect resulting from them in changing the condition of men and things." That task of illumination has often been accomplished in greater or less detail by historians of science and by economists. Equally important, however, is the task, somewhat neglected, of tracing the influence of scientific discoveries and the development of scientific theories upon human thought. That formidable task may perhaps be attempted for the present purpose in bare outline by undertaking a brief survey of the reflections of science in literature through the ages.

Man's Earliest Literature

The association between literature and science may be traced back to remote times when each of these two great fields of human thought and endeavour existed only in a rudimentary form. Even the Ebers Papyrus, the so-called "oldest book in the world," written some thirty-five centuries ago in a cursive form of the chiseled hieroglyphs of ancient Egypt, has a strong scientific interest. Through the earlier labors on the Rosetta Stone of the eminent physicist, Thomas Young, conjoined with those of Champollion, it became possible to identify the Ebers Papyrus as a primitive pharmacopoeia, and to reveal its strange collection of more than eight hundred prescriptions and remedies.

Dating from much later, about the seventh century B.C., and still extant, are numerous Babylonian tablets from the royal library of the Assyrian king, Assurbanipal; these are inscribed with practical information concerning what would now be called the technology of metals, glass, and other materials. Other tablets of this kind date from a much earlier period. Noyes, in his poem, "The Torch-Bearers," refers to records of these ancient days when he writes:

> The eclipses timed in Babylon help us now
> To clock that gradual quickening of the moon,
> Ten seconds in a century. Who that wrote
> On those clay tablets could foresee his gift
> To future ages?

Aristotle, in the fourth century B.C., held that matter was continuous and capable of infinite subdivision. Epicurus, somewhat later, revived the atomistic speculation of earlier Greek philosophers, according to which matter is discontinuous or grained. This Epicurean philosophy was expounded in the first century B.C. with passionate eloquence and power by the Roman poet Lucretius. His didactic poem *De Rerum Natura* ("Concerning the Nature of Things") expounds the thesis that the gods, like men, are mortal, and that the atom alone throughout the universe is eternal and incorruptible. This jewel of Latin literature is the earliest literary work of the first rank which deals with science.

Of Tyrian purple, the imperial colour, the most precious dye of the ancient world, Lucretius wrote:

> The purple dye of the shellfish so unites with the body of wool alone, that it cannot in any way be severed, not were you to take pains to undo what is done with Neptune's wave, not if the whole sea were willed to wash it out with all its waters.

Returning to this theme two thousand years later, Robert Browning exclaimed:

> Who has not heard how Tyrian shells
> Enclosed the blue, that dye of dyes,
> Whereof one drop worked miracles,
> And coloured like Astarte's eyes,
> Raw silk the merchant sells?

There was much intermingling of the mathematical and scientific knowledge and ideas of ancient Greece with those of Persia and Syria, a fuller co-ordination of which took place in Hellenistic Egypt. From about the seventh century A.D. this corpus of knowledge and ideas passed to Islam; and eventually the accumulated knowledge of the Muslim mathematicians, astronomers, medical men, alchemists, and other protagonists of early science, drawn from various sources and augmented during its passage through Islam, percolated into Western Europe.

This passage westward occurred chiefly through Spain, and in the form of Latin translations of Arabic texts. Among the translators were the Englishmen, Robert of Chester and Adelard of Bath, and the Scotsman, Michael Scot. These were pioneers in introducing science into Britain in a literary form, albeit in Latin.

The cover

Dr. Sidney M. Edelstein, secretary of the ACS Division of History of Chemistry, presents the Dexter Award to Prof. John Read at a meeting of the British Chemical Society. Prof. Harry Julius Emeleus (left), president of the Chemical Society (London) also participated in the ceremony.

Prof. Read, whose research interests have been in the field of stereo chemistry, is widely known as a teacher, historian, and author. His pen has contributed notably to illuminating the humanistic values of science.

[1] READ, JOHN, "Humour and Humanism in Chemistry," G. Bell & Sons, London, 1947, p. 161; "Humor y Humanismo en la Quimica," Aguilar, Madrid, 1953, p. 164.

Dominating Position of Alchemy

The translators of the twelfth century were succeeded by the encyclopaedists of the thirteenth, whose role was to collect and edit, in manuscript form, the knowledge that had come through to them from ancient Greece and other eastern sources. One of the greatest of these scholastic philosophers, as his name indicates, was Albertus Magnus (1193–1282), also known as *Doctor Universalis*. Some of the Latin scripts were translated into English. There is, for example, in the British Museum, an English manuscript version written in the fifteenth century, of the *Semita Recta* ("Straight Path") an alchemical tract attributed to Albertus. This states that

> "alle metaills been ingendard in therthe of sulphur and mercury . . .Whene reede sulphur and pure and not brennyng renneth in therthe with mercury thereof is ingendrid gold. . .but whene white sulphur renneth to mercury in cleene erthe thereof is ingendrid silvre and hit hath noo difference fro gold but that sulphur in gold is not corrupte but in silvre hit is corrupte."

This manuscript offers an indication of the dominating position of alchemy in the literature of early science. Enduring for more than a thousand years, from the early Christian era until late in the seventeenth century, alchemy was not merely the forerunner of chemistry, animated by visions of the Philosopher's Stone and the *Elixir Vitae*, with their concomitants of wealth and long life. This exoteric alchemy, indeed, was no more than the materialistic phase of a great philosophical system, based upon an esoteric, or spiritual, alchemy. As an integral part of this large system, exoteric, or practical, alchemy took its place beside philosophy, religion, mysticism, astrology, theosophy, and many other elements. In the Middle Ages and later the conceptions and imagery of this larger alchemy found in contemporary literature and art a wide expression of which there is little realization at present. Moreover, the great ocean of alchemical literature, written and printed in many languages, remains a closed book, a book both closed and hermetically sealed, to the literary specialists of our own day.

Much of this literature, in particular of the esoteric kind, is very difficult to interpret. It may be said, however, that according to the fundamental tenets of alchemy, matter possesses an essential unity; the common soul of matter alone is permanent, the body, or outward form, being transitory and transmutable. The sulphur-mercury theory of the constitution of metals, already adumbrated, regards the properties of matter as separate from matter itself. "Sulphur" is merely a name for the property, or principle, of combustibility; "mercury" is the property, or principle, of metallicity and fusibility. The incorporation with matter of these principles in an impure state leads to base metals; in purer states to the noble metals, silver and gold; and in superfine states to the Philosopher's Stone. Sometimes in the Great Work of preparing this potent transmuting agent a third principle, known by such names as "salt" and "magnesia," was considered necessary.

An interesting impression of some of the contributions in English to alchemical literature may be gained from Elias Ashmole's collection of twenty-nine English alchemical writings in verse, which he published in 1652 under the title "Theatrum Chemicum Britannicum." Chief among them are Norton's "Ordinall of Alchimy," Ripley's "Compound of Alchymie," and " 'The Tale of the Chanons Yeoman,' written by our Ancient and famous English Poet Geoffry Chaucer."

The esoteric alchemists were usually deeply imbued with religion, so that their writings abound in references to religious beliefs and doctrines, including, for example, repeated associations of the Christian mystery of the Trinity with the alchemical mystery of the triune Stone. In one of Ashmole's poems, rescued, as he says, "from that Universall Deluge, which (at the Dissolution of Abbies) overflowed our greatest Libraries," the constituents of the Stone are likened to the gold, frankincense, and myrrh of the three Magi:

> Aurum betokeneth heer, owre Bodi than,
> The wych was brought to God and Man,
> And Tus alleso owre Soul of lyfe,
> With Myrham owre Mercurye that ys hys Wife.
> Here be the thre namys fayre and good
> And alle thaye ben but one in mode.
> Lyke as the Trinite ys but on,
> Ryght so conclude the *Phylosofeers Stone.*

Among the minor pieces of Ashmole's collection is a charming little poetical tribute to the magical herb called Lunary, or Moonwort, endowed by alchemists with particular virtues because of the likeness to the crescent moon which they perceived in the shape of its leaves:

> Her ys an Erbe men calls *Lunayrie*
> I-blesset mowte hys maker bee. .
> The Levvis ben rownd, as a Nowbel son,
> And wexsyth and wanyth as the Mon:
> In the meddis a marke the brede of a peni,
> Lo thys is lyke to owre sweght Lunayre.

Chaucer and Norton

Of the major items, those of Chaucer and Norton call for particular notice. Although these two literary presentments of alchemy are separated in time by about a century, they depict in a sense two contemporary aspects of an essentially static subject.

It is fortunate for all who value the literary and humanistic associations of science that Geoffrey Chaucer, "the father of English poetry," devoted one of his "Canterbury Tales" to a delineation of the alchemy of his day; for in the "Canon's Yeoman's Tale" the Canon is an alchemist and the Yeoman is his assistant "labourer in the fire." In this narrative, alive with humanity and illumined with literary charm, Chaucer gives a genre picture of an alchemical laboratory, its denizens, and its goings-on, as vivid and faithful as the later representations, in another medium, of that artist of alchemy *par excellence*, David Teniers the Younger. This "Tale," indeed, is the finest and best known literary work dealing in any language with medieval alchemy.

Chaucer's treatment shows the master-hand of an imaginative poet of the first rank who possessed also an intimate knowledge of the science of his day; indeed, his unfinished "Treatise on the Astrolabe" (1391) was probably contemporaneous with the "Canon's Yeoman's Tale." Of the two Canons under whom the Yeoman served, the first was an uninformed alchemist

of the lowest exoteric type and the second was a pure charlatan and impostor. There is much in this "Tale" showing that the subjective human aspect of the laboratory has changed little in the last six hundred years. Let us "listen in" to one of the many laments of the sorely-tried Yeoman:

> Whan we be ther where we shul exercise
> Oure elvish craft, we seme wondrous wyse,
> Oure termes be so lerned and so queynte.
> I blow the fyr til that myn herte feynte.
> And wit ye how? Ful ofte it happeth so,
> The pot to-breketh, and farwel, al is go. . .
> There never was suche wo or anger or ire
> As when our pot is broke, as I have sayd,
> Every man chideth, and thinketh him ill paid.
> Some sayd it was too long on the fyr-making;
> Some sayde nay, it was on the blowing;
> (Than was I feared, for that was myn office).

Thomas Norton of Bristol was an alchemical adept, endowed alike with a full esoteric knowledge and practical experience of alchemy; according to tradition he was a pupil of the celebrated George Ripley, Canon of Bridlington. Norton was an early member of a long sequence of scientists with poetic tendencies. His "Ordinall of Alchimy," begun in 1477, a long poem consisting of seven chapters following a Probeme, has perhaps no great literary merit, although Norton is "usually able to scramble home with a rhyme at the end of his line." The archaic language of the poem is attractive, and its account of the beliefs and practices of fifteenth-century alchemy is of great historical value. Norton stresses the esoteric nature of "holi Alchimy," the secrets of which are imparted only under the seal of a "most sacred dreadful Oath:"

> Almighty God
> From great Doctours hath this *Science* forbod.
> And graunted it to a few Men of his mercy,
> Such as be faithful trew and lowly.

The poem shows Norton as a capable laborant and director of practical operations. Like all alchemists he had his trials, and he suffered from the incompetence, "deceipt," and dishonesty of those around him. At one point he was deprived of the result of much labour,

> For when I had my warke well wrought
> Such stale it away and left me nought.

An even greater misfortune befell him when a fair deceiver, the wife of a Bristol merchant, purloined his Elixir of Life, as he says,

> To my greate paine and much more woe:
> Soe in this worke there is no more to saine,
> But that every *Joy* is medled with his paine.

Ben Jonson and Shakespeare

In alchemy, time stood at gaze. Although Ben Jonson's famous play, "The Alchemist," was written more than two hundred years after Chaucer's masterpiece, the central figure, Subtle, like Chaucer's second Canon, is a "cheater" and "coz'ner at large," and an alchemist only by courtesy. Naturally, also, that *ignis fatuus* of alchemy, the Philosopher's Stone, lies again at the heart of the scene. "This day I am to perfect for him," says Subtle of Sir Epicure Mammon,

> The magisterium, our great work, the stone:
> And yield it, made, into his hands; of which
> He has, this month, talked as if he were possessed.

Jonson's play pilloried the familiar chicaneries, frauds, credulities, and superstitions of Jacobean London. Laden with telling wit and biting satire, it made a lasting appeal to the audiences of that age. Much later, in 1661, after the Restoration, Pepys lauded it in his diary as "a most incomparable play." In still later ages, although its alchemical ideas, imagery, and vocabulary had become largely obsolete, Coleridge described its plot as one of the three most perfect ever planned; and Swinburne ranked it as unique and among "the greatest of comic triumphs ever accomplished." As I have written elsewhere,[2] Jonson's "lavish transmutation of alchemical imagery and expressions in this great work of English literature envelops the play in a poetic web of great beauty; at the same time, his command of these alchemical technicalities is so consummate that 'The Alchemist' is one of the best and most accurate repositories of the ideas and vocabulary of seventeenth-century alchemy."

This later period of alchemy was marked by many extravagances, among them the quaint conception that the whole corpus of classical mythology had been designed expressly to record in a concealed and allegorical form the secret doctrines of the so-called "sons of Hermes," or alchemical adepts.[3] Jonson makes great and eloquent play with such classical allusions, in describing what he calls "the manner of our work:"

> The bulls, our furnace,
> Still breathing fire: our argent-vive, the dragon:
> The dragon's teeth, mercury sublimate,
> That keeps the whiteness, hardness and the biting;
> And they are gathered into Jason's helm,
> (The alembic), and then sowed in Mars his field,
> And thence sublimed so often, till they're fixed
> Both this, th' Hesperian garden, Cadmus' story,
> Jove's shower, the boon of Midas, Argus' eyes,
> Boccace his Demogorgon, thousands more,
> All abstract riddles of our stone.

Although Shakespeare evinced no outstanding interest in the science of his day, he wrote of the dawning sun "gilding pale streams with heavenly alchemy." Also, he alluded repeatedly to "the tinct and multiplying medicine," the "medicine potable," "that great medicine," which in the words of Cleopatra to Alexas, "hath with his tinct gilded thee." He deplored the application in warfare of that "villainous saltpetre . . . which many a good tall fellow had destroyed so cowardly"; and in the field of celestial mechanics he based some of his most eloquent poetic imagery upon the ancient Pythagorean conception of the music of the spheres.

Nevertheless, there is no doubt that Shakespeare, no less than Ben Jonson and other contemporary writers, was acquainted with Thomas Digges' "Perfect Description of the Celestial Orbs," a Copernican treatise first printed in 1576 and reissued five times within the next twenty years. But Shakespeare, like others, found little difficulty in accommodating old beliefs of the Ptolemaic or geocentric system in a new framework of the Copernican or heliocentric system of which Digges

[2] READ, JOHN, "The Alchemist in Life, Literature and Art," Thos. Nelson & Sons, London and Edinburgh, 1947, p. 40.

[3] READ, JOHN, "Prelude to Chemistry," G. Bell & Sons, London, 1936, p. 234; The Macmillan Co., New York, 1937, p. 234.

himself proclaimed, "we may behold such a wonderful symmetry of motions and situations as in no other can be proponed."

Thus, in "A Midsummer-Night's Dream" Shakespeare alludes to "certain stars" that "shot madly from their spheres, to hear the sea-maid's music"; and a beautiful passage in "The Merchant of Venice" runs in this wise:

> Look how the floor of heaven
> Is thick inlaid with patines of bright gold:
> There's not the smallest orb which thou behold'st
> But in his motion like an angel sings,
> Still quiring to the young-eyed cherubins;
> Such harmony is in immortal souls;
> But whilst this muddy vesture of decay
> Doth grossly close it in, we cannot hear it.

As a footnote to these astronomical allusions it may be said that there is evidence that Shakespeare probably saw in the house of the aforementioned Thomas Digges, who was a friend of Tycho Brahé, an engraved portrait of this celebrated Danish astronomer containing certain ancestral names, of which two appear in "Hamlet" as the courtiers Rosencrantz and Guildenstern.

Shakespeare and Ben Jonson were born in the latter half of a century which had already seen great changes in science. At the time of the writing of "The Alchemist," alchemy had passed its zenith and had entered upon a period of decay. Almost a century earlier, Paracelsus had endeavoured to give a new direction to alchemy by allying it with medicine, and in Ben Jonson's day the old alchemy was pursuing a downward course while its new orientation gathered force. The seventeenth century thus witnessed the rise and development of a species of medico-chemistry, known also as iatrochemistry, and sometimes as chymistry. This diversion of alchemy was symptomatic of a much wider and deeper movement.

The opening of that momentous sixteenth century of Shakespeare and Jonson, at which time Paracelsus was a youth at Einsiedeln, had been "marked by a great forward surge of the Renissance, that transitional movement in Europe between the medieval and modern order of Western civilization. Many diverse influences were coming at that time into a common focus. Among them, the impact of the wonderful flood of rediscovered classical knowledge was gathering force; the power of the new art of printing was beginning to take effect; and the confines of the known world were rapidly expanding as a consequence of the voyages of Columbus (1492), Vasco da Gama (1497), and Magellan (1521). Fresh horizons of the material and intellectual world were opening with a rapidity hitherto unknown. Doctrines and conceptions that had held fast throughout the rigid period of medievalism now began to be questioned and assailed."[4]

In this new and stimulating atmosphere there arose many pioneers of a fresh order. Early among them came Luther, whose success in the struggle to burst the bonds of religious orthodoxy and tyrannic authority found a dramatic expression in his public burning of the Papal Bull of Condemnation at Wittenberg, in 1520. Seven years later, Paracelsus similarly condemned the orthodox system of medicine by publicly consigning the venerated writings of Galen and Avicenna to the flames in the market-place of Basel. Sixteen years later still, two more significant upheavals in science found expression in two great works printed in 1543. Copernicus' *De Revolutionibus Orbium Coelestium* revolutionized the most ancient of sciences by asserting that the earth was a planet revolving around the sun, instead of being the hub of the universe, as depicted in the hoary Ptolemaic system of the second century A.D.; and Vesalius' *De Fabrica*, the foundation work of anatomy, brought about an advance of equal importance in biology.

[4] READ, JOHN, "Through Alchemy to Chemistry," G. Bell & Sons, London, 1957, p. 95; "De l'Alchimie à la Chimie," Arthème Fayard, Paris, 1959, p. 141.

Scientific Revolution of the Seventeenth Century

And so the dawn of the seventeenth century, the day of the rich English literature of Shakespeare, Ben Jonson, Burton, Donne, Campion, and many another, brought with it the dawn of the so-called "scientific revolution," and thereby heralded the birth of modern science. The scientific revolution of the seventeenth century hinged upon astronomy, the oldest of the sciences, and found its inspiration in the law of inertia. The ideas of Galileo (1564–1642) concerning mass and inertia formed the foundation of the first law of motion, as enunciated by Newton (1642–1727), who was born in the year of Galileo's death. Nearly a century and a half after Copernicus' *De Revolutionibus Orbium* (1543), Newton was able in his *Principia* (1687) to effect his grand synthesis of the fundamental dynamical and gravitational problems concerned in the motions of the heavenly bodies. This correlation of dynamics and astronomy, of motion on the earth and in the skies, of the falling apple and the falling moon, lies at the very core of the scientific revolution of the seventeenth century.

Newton's theory of gravitation at once superseded the short-lived vortical theory of Descartes (1596–1650), the great philosopher and mathematician whose *Discours de la méthode* (1637) and axioms ("cogito: ergo sum"; "whatever is clearly and distinctly thought must be true") exerted so great an influence upon the thought of his own and a later age.

In another, widely removed, field of science, Vesalius' masterwork of anatomy, *De Fabrica* (1543), was followed in due course by William Harvey's revolutionary work, *De motu cordis* (1628), dealing with his discovery of the circulation of the blood. A new era had opened also in the study of living organisms.

How many students of the arts—indeed, how many students of the sciences—realize that the scientific revolution, this most fundamental of all changes in human thought, was due in the first place to Italy and found a focal point in the University of Padua? This seat of learning, so ancient and so rich in fame, claimed close associations with Copernicus and Galileo, and it had been mightily enriched by the work of Vesalius and of Harvey's own teacher, the great Fabricius.

Now the scientific view of the enormous advances here so hastily sketched represents only one aspect of the scientific revolution. That revolution had a much wider significance. The new conception of a macrocosm subject to dynamical laws and no longer impelled by invisible hands, and the new knowledge of the living microcosm of man, exerted a profound influence upon

the society and general mental attitude of the day. Here is an example of the truism, so important and yet so often overlooked, that the history of science does not exist as an immiscible layer floating upon the stream of general history; but that it is an all-pervading and vivifying ingredient of that stream.

Reaching maturity in the early days of this revolution in scientific thought, Francis Bacon (1561–1626), a great literary figure, is best known to the general reader as the author of the classical essays. Among scientists he deserves equal renown as the author of the *Novum Organum Scientiarum* (1620) and founder of the inductive system of philosophy, based upon experiment, observation, and measurement, of which Robert Boyle was one of the first eminent exponents. Of his contemporaries in English literature, few evidenced any inkling of the coming impact of the scientific revolution upon the whole current of human thought. Perhaps it is not too much to claim that only the two greatest poets of that age, Donne and Milton, had a glimpse of the impending change. "The new philosophy calls all in doubt," wrote Donne. As for Milton, although he adopted the ancient Ptolemaic system in his great epic "Paradise Lost," there is no doubt that he was well acquainted with the informed contemporary view; and he had indeed visited the "famous Galileo, grown old."

The Royal Society

It was not until after the upheavals of the Civil War and the unease of the Commonwealth that science and literature were brought into close relationship in England, with the foundation of The Royal Society by King Charles II in 1660. This most famous of all scientific societies, set out with the avowed aim of improving and enlarging "the empire of operative philosophy by the real effects of the experimental." It is significant that among its early members eminent scientists of the calibre of Boyle, Hooke, and Newton mingled with men of letters like Evelyn, Waller, Cowley, Dryden, and Pepys, and that Christopher Wren was one of the early presidents. This intimate association gave impetus to the profound change that was now penetrating through contemporary literature to the general thought of the new epoch, a change that has been described as a shifting of values from the next world to this.

Moreover, this interplay of science and literature infused a new style into literary writings. From the days of Chaucer, the vocabulary of science had infiltrated gradually into the English language, but science was now destined to influence increasingly the method of literary expression. The Royal Society insisted upon "a close natural way of speaking, positive expressions, clear senses, a native easiness, bringing all things as near the mathematical plainness as possible." Contemporary writers caught this fashion to such a degree that Dryden, expressing his independence of outlook in his work "Annus Mirabilis," wrote "My whole discourse is sceptical, according to the way of reasoning initiated in the modern inquisition of the Royal Society."

It would be wrong however to depict writers of that day as subservient to the Royal Society. While learning from the Society they often administered a wholesome corrective to the excesses of its Fellows, some of whom were given to trivialities and extravagances. To be a member of a Society owning the King as patron carried a cachet which attracted many so-called virtuosi, amateurs of science whose uninformed activities and writings tended to bring discredit upon the learned academy to which they belonged. Samuel Butler, the lively-minded author of "Hudibras," wrote a particularly pungent and amusing skit which described a group of these virtuosi gazing through a telescope at a great battle on the moon, in which a monstrous elephant played havoc among the lesser combatants; only to find, after entering their account in the *Transactions*, that the fighting men were flies on the lens, and that the elephant was "a mouse that, by mishap, had caught himself, and them, in the optic trap."

At a later date Swift was equally devastating in his satirical description of Gulliver's encounter at the College of Lagado with learned professors engaged in such pursuits as extracting sunbeams from cucumbers; moreover, he concocted an ingenious analogy between the different grades of poets and the wonders of the microscopic world, which had been first laid bare in Hooke's "Micrographia":

> So Naturalists observe a flea
> Has smaller fleas that on him prey;
> And these have smaller fleas to bite 'em
> And so proceed *ad infinitum*.

At this time, in the early years of the eighteenth century, it became a popular pastime among men of letters to poke fun at scientists and to satirize them and their publications. Swift must have devoted serious study to astronomy, before attributing to the astronomers of Laputa the discovery of two satellites of Mars, an extraordinary speculation which was verified in 1877. Perhaps, however, it was Addison, of all the writers of that period, who had the greatest feeling for science; he and Steele certainly catered in their periodicals to readers having an interest in this fashionable subject, the *dernier cri* of that day.

The general tendency in the literature of this dawn of the "Age of Reason," a tendency induced by the mechanistic view of the universe, was an endeavour to rationalize religious beliefs. Richard Bentley, the great Cambridge scholar and critic, actually applied to Newton in support of Christianity, and derived satisfaction from Newton's reply that

> "the planetary system argues a first cause not blind and fortuitous, but very well skilled in mechanics and geometry."

There was little in Newton's reply, as generally in the writings of that age, to satisfy the longings of a soul in search of God. As Archbishop William Temple wrote some two centuries later:

> "Science aims at explaining the world—that is, making it satisfactory to the mind. . .But the mind is not only logical, but also moral, and will not be content with an account of the world which does not demonstrate its morality."

The new knowledge became so much of a vogue in this era that attempts were made by writers in various countries to bring it before the reading public in simple and understandable terms. First and foremost among them was Fontenelle, nephew of Corneille, and in Voltaire's opinion the most universal genius of his day.

Living to within a month of his century (1657–1757), this remarkable man spanned the passage from the scientific revolution of the seventeenth century to the "Age of Reason" of the eighteenth. His charming book entitled *Entretiens sur la pluralité des mondes* was first published in 1686, and it was translated into English as "Conversations on the Plurality of Worlds." Fontenelle's method of brightening science was to expound it to a lovely countess in a beautiful garden by moonlight. They look at the heavens, and the expositor observes that "Philosophy is now become so mechanical that they will have the World to be in Large what a Watch is in small." The countess replies, "I value it the more since I know that it resembles a Watch, and the more plain and easy the whole order of Nature seems to be, to me it appears the more admirable."

By the side of Fontenelle we may place the Italian, Algarotti, who, in 1732 gave an equally attractive exposition, to a charming Marchesa, of the latest theories of light in his book, *Il Newtonianismo per le Dame*. A typical English work of the same kind appeared later under the title, "The Young Gentleman and Lady's Philosophy, in a continued survey of the Works of Nature and Art; By Way of Dialogue."

Birth of Modern Chemistry

It is a remarkably significant fact, both in historical science and in the development of our modern civilization, that the scientific revolution of the seventeenth century stopped short at chemistry: this because chemistry is based fundamentally upon obscure principles, the elucidation of which came very slowly after prolonged speculation and experiment. As early as 1674, John Mayow, a young Cornishman who practiced medicine at Bath, had carried out some remarkable investigations on the fundamental problems of combustion and respiration; but no appreciable advance upon the work and views of Boyle, Hooke, and Mayow in the later seventeenth century was found possible for another hundred years, owing largely to lack of knowledge of ways of manipulating and characterizing gases, all of which were regarded at that time as ordinary air in different states of purity. Meanwhile chemical thought was dominated by a misleading theory, according to which a burning body emitted an imaginary principle called phlogiston. Suddenly, however, in the second half of the eighteenth century, a great change came over the chemical scene, when the combined researches of Black, Scheele, Priestley, and Cavendish enabled Lavoisier to put forward the modern interpretation of burning, or combustion, as combination with a gaseous component of the atmosphere. This was discovered by Priestley in 1774 and later named oxygen by Lavoisier. With the substitution of the positive oxygen theory for the negative theory of phlogiston, modern chemistry was born. Soon afterward, in 1808, "the abolition of the old ideas and the accumulation of accurate quantitative data led to the formulation by John Dalton of that comprehensive Atomic Theory whose innumerable ramifications form the nervous system of the wonderful body of physical science as we know it today."[5]

From the later decades of the eighteenth century onward applied chemistry also made rapid advances. The development of the heavy-chemical industries set in with improved methods for the large-scale manufacture of sulfuric acid, the discovery of the Leblanc process for making soda, the advent of bleaching powder, and many associated advances in allied industries. In another field of chemistry the introduction of coal gas as an illuminant, in 1792, foreshadowed the birth of organic chemistry and of its great industries based upon coal tar.

The acceleration in the progress of science and its application to industry, synchronizing with the invention of Watt's steam-engine, Cartwright's power-loom, and other mechanical devices led to the so-called industrial revolution in Britain. The growth of factories, the concentration of population in the coal areas, and the decline of agriculture brought about great changes in the social structure of the country. At the same time the further discoveries and ideas of Erasmus Darwin, Davy, and other scientists and thinkers justified Erasmus Darwin's pronouncement that they "enlisted Imagination under the banner of Science."

The Romantic Movement and Science

This world of speculation and revolutionary thought witnessed a literary renaissance known as the Romantic Movement, in which Wordsworth (1770–1850) was the leader and outstanding figure of a school including such famous poets of the time as Keats, Coleridge, and Shelley. The earlier English poets, notably Dryden and Pope, had written in the classical style of Latin poetry; they dealt, often satirically, with society, politics, and moral theories, regarding man's life objectively, and relegating Nature to gardens and artificial pastorals. The new Romantic poetry, heralded by such forerunners as Crabbe, Cowper, and Blake, sought inspiration, both in lyrical and dramatic form, in the common feelings and ideas of ordinary folk, and in Nature. The style was characterized by simple language, with a variety of meters replacing the former heroic couplet.

The Romantic Movement was induced by the mechanistic nature of scientific theory and the growing revolt of the aesthetic sense against the effects of the industrial revolution; it came as a literary reaction against materialism, a reaction sustained also by neo-Platonic ideas, and its participants found refreshment in turning from the ugliness of factory and mine to a contemplation of rustic life and the calm delights of Nature. At the same time it may be held that in Shelley, the poet, as in Newton, the scientist, there was no impassable gulf between science and neo-Platonism.

Wordsworth, perhaps more than any other poet, gave his soul to Nature; and the spirit of the Romantic revival was that of a return to *real* nature, in contrast to Dr. Johnson's *rational* nature of the preceding "Age of Reason." Wordsworth brooded in his poetry over the profound problem of the relation of scientific thought to the spiritual life. He viewed man as a spiritual being in whom poetry and all that it represents should come before science, seeing that true poetry raises thought and feeling into a higher region of imagination which is the home of the spiritual life. How-

[5] READ, JOHN, AND GUNSTONE, FRANK D., "A Text-Book of Organic Chemistry," G. Bell & Sons, London, 1958, p. 26.

ever, Wordsworth, "the poet of Nature and of Man," must not be regarded as opposed to science and scientists; indeed, as he makes clear in "The Prelude," one of his abiding memories of Cambridge was of

> Where the statue stood
> Of Newton, with his prism and silent face,
> The marble index of a mind forever
> Voyaging through strange seas of thought alone.

To Wordsworth, poet and scientist were "twin labourers, and heirs to the same hopes," and he gloried in the achievements of mathematics with "its independent world, created out of pure intelligence." His liberal attitude of mind finds expression in his lines:

> Happy is he who lives to understand
> Not human nature only, but explores
> All natures,—to the end that he may find
> The law that governs each.

The interplay at this time between science and literature was personified in the close friendship existing between Coleridge and Humphry Davy, of whom Coleridge said that "if Davy had not been the first Chemist, he would have been the first Poet of his age." Davy was a friend also of Sir Walter Scott, and Lockhart records an occasion at Abbotsford when "the modesty of their mutual admiration was a memorable spectacle." Upon another occasion, in 1805, Lockhart, in referring to a meeting of Davy and Scott in the Lake District, wrote: "I have heard Mr. Wordsworth say, that it would be difficult to express the feelings with which he, who so often had climbed Helvellyn alone, found himself standing on its summit with two such men as Scott and Davy."

Nineteenth Century: Intellectual Readjustment

Wordsworth died in 1850. Nine years later Charles Darwin published his epoch-making work on the "Origin of Species," of which Huxley said: "It is doubtful whether any other single book, except Newton's *Principia*, has worked so great and so rapid a revolution in science, or made so deep an impression on the general mind." Darwin expounded his evolutionary theory with a literary clarity which also distinguished the writings of T. H. Huxley and other contemporary scientists. These writings shook the foundations of religious belief and brought forth a great literature, for literature must inevitably keep abreast of fundamental advances in scientific thought and of the effects of scientific discovery on social conditions.

There ensued a period of intense intellectual doubt and readjustment. Of the great literary figures of the Darwinian period, some—in particular Carlyle—affected to ignore the birth of a new epoch; others, including Arnold, Clough, and George Eliot, were baffled in trying to reconcile the claims of science and religion in this new chapter in the story of man; Meredith accepted the evolutionary doctrine with a buoyant optimism, but among them all, Tennyson stood out as the great interpreter of the mood of that troubled age.

Tennyson, like his contemporaries, Robert Browning and Matthew Arnold, was deeply interested in science, particularly in astronomy. In his poetical references to the starry heavens he blends lyrical beauty with scientific truth:

> Many a night from yonder ivied casement, ere I went to rest,
> Did I look on great Orion sloping slowly to the West.
> Many a night I saw the Pleiads, rising through the mellow shade,
> Glitter like a swarm of fire-flies tangled in a silver braid.

In some respects Tennyson even anticipated Darwin's statement of evolutionary doctrine; moreover, according to the scientist, Romanes, he recognized the operation of Natural Selection in advance of Darwin. Holding to his beliefs on immortality and Christianity, he realized that science is not immutable and that human knowledge is restricted:

> Our little systems have their day,
> They have their day and cease to be:
> They are but broken lights of thee,
> And thou, O Lord, art more than they.

Until the coming of fuller knowledge, Tennyson foresaw no reconciliation between Faith and Science: each had its own sphere, and meanwhile Faith stood beyond either proof or disproof. As the eminent physicist, Andrade, has expressed it in our own day: "Science has proof but no certainty: religion has certainty but no proof."

In the earlier words of Goethe, the only supreme poet who having a practical acquaintance with science, sought out truth in general:

> "The greatest happiness of the thinking man is to have fathomed those things which are fathomable, and to reserve those which are unfathomable for reverence in quietude."

Tennyson welcomed scientific discovery, and to him evolution implied progress based upon the steadying influence of tradition. As he proclaimed in "Locksley Hall," he

> rather held it better men should perish one by one,
> Than that earth should stand at gaze like Joshua's moon in Ajalon!
> Not in vain the distance beacons. Forward, forward let us range,
> Let the great world spin for ever down the ringing grooves of change.
> Thro' the shadow of the globe we sweep into the younger day:
> Better fifty years of Europe than a cycle of Cathay.

In contrast to the mild optimism of Tennyson and Meredith stand the tragic questionings of Thomas Hardy, with his insistence upon a helpless insignificance of the individual that is only stressed by the evolutionary progress of the type. The chronic melancholy which is taking hold of the civilized races with the decline in the belief of a beneficent Power, as he expresses it in "Tess of the D'Urbervilles," falls into line in his philosophy with that indifferent ruling force of that greatest of all his works, "The Dynasts":

> Like a knitter drowsed,
> Whose fingers play in skilled unmindfulness,
> The Will has woven with an absent heed
> Since life first was, and ever so will weave.

Hardy, taking first rank as novelist, poet, historian, and philosopher, also evinced a lively interest in science. He enjoyed bringing his perceptive mind to bear upon intelligible expositions even of its abstruse branches. "Tell me in simple language what you are doing just now in organic chemistry," he said to me on one of my visits to him at Max Gate, Dorchester, in the 1920's; and he showed a remarkable appreciation of a field of discussion ranging from the nature of right- and left-

handed molecules to asymmetric physiological action and the direction of the spirals of climbing plants. One of his penetrating questions I may record. "Here in Dorset," he said, "the sun passes from east through south to west, and the runner bean climbs in a dextral spiral. Have you noticed whether it takes on a sinistral spiral in Australia, where the sun passes from east through north to west?"

What of the Twentieth Century?

The widespread development of science has become increasingly evident in the literature of the twentieth century, particularly in the writings of men with scientific training. In this field, H. G. Wells, with his blend of scientific and creative instincts, attained a prominent place with his imaginative novels and his studies of contemporary social life and problems. In a different field, Henry Havelock Ellis displayed a literary instinct in his remarkable psychological and sociological works. Psychology is fast attaining the status of a science, and the influence of such psychologists as Freud and Jung upon modern literature and thought is manifest. Typical of later imaginative novels by authors with scientific and technological insight are Nevil Shute's "No Highway" and Nigel Balchin's "Small Back Room." The popularizers of science, also—the modern Fontenelles—have included such scientific specialists as Eddington and Jeans, with their expositions of current views of the universe.

Science has been claimed to foster a curious literary style of the modern epoch, based essentially upon the habit of Lewis Carroll (C. L. Dodgson), the creator of "Alice," in using words, much as in another context he used mathematical symbols. This tendency found a clear expression in Ezra Pound's statement that "poetry is a sort of inspired mathematics, which gives equations, not for abstract figures, triangles, spheres, and the like, but equations for human emotions."

There is naturally a tendency to introduce specialized scientific words into the vocabulary of the poet and imaginative writer; but a contemporary scientist, P. E. Spielmann, in commenting from this point of view upon the writings of James Joyce and Henry Crosby, remarked that "in a poem by the latter all the words are completely new, completely incomprehensible," adding that

> "this separation of a word from any meaning evidently links with the 'abstract-making' mentality of the artist that attaches more importance to the curve than to the body from which it was taken, and also connects with the alchemists who tried to separate the properties of matter from matter itself."

Here we find a scientist concluding that the contemporary arts in general—pictorial art, architecture, music, poetry— have been changed "by the unjustifiable application of scientific theory to the roots of artistic creation . . . with loss of beauty and emotion." On the other side of the tree of scientific knowledge, bearing fruit of such exceeding bitterness, stands the man of letters, Aldous Huxley, offering in his book "Ape and Essence" a merciless satire on both science and human-kind in this "atomic age."

Some time ago I wrote that "the intimate chemical and physical knowledge that man has now acquired of his environment represents the greatest of all his intellectual achievements": pointing out, however, that in order to gather the fruit of this great tree of knowledge he "must learn to master and control himself as he has learned to master and control nature."[6]

There is no natural law preventing him from so doing. When he attains this consummation, for which all must hope and work, man will at last witness the realization of the eloquent prophecy of Isaiah:

> "The wilderness and solitary place shall be glad for them; and the desert shall rejoice and blossom as the rose. . .Then the eyes of the blind shall be opened, and the ears of the deaf shall be unstopped. Then shall the lame man leap as an hart and the tongue of the dumb sing, for in the wilderness shall waters break out, and streams in the desert. . .They shall obtain joy and gladness, and sorrow and sighing shall flee away."

[6] NEWMAN, JAMES R. (ed.), "What is Science?" Simon & Schuster, New York, 1955, p. 194.

Nominations for 1960 Dexter Award

Nominations are being solicited for the 1960 Dexter Award in the history of chemistry administered by the Division of History of Chemistry of the ACS. The Award consists of a suitable plaque and $500.00.

"The Award shall be made on the basis of services which have advanced the history of chemistry in any of the following ways: by the publication of an important book or article; by the furtherance of the teaching of the history of chemistry; by significant contributions to the bibliography of the history of chemistry; or by meritorious services over a long period of time which have resulted in the advancement of the history of chemistry."

All information, in duplicate, should be sent to the secretary of the Division of History of Chemistry, Dr. Sidney M. Edelstein, Dexter Chemical Corporation, 845 Edgewater Road, Bronx 59, N. Y.

H. Bradford Thompson
Gustavus Adolphus College
St. Peter, Minnesota

Dynamic Projector Display for Atomic Orbitals and the Covalent Bond

Every teacher has to stretch the truth a little in the preliminary presentation of complex ideas. However, simplifications should be used only if they truly simplify learning; out-of-date "pictures" of atomic electrons often fail to do this. Electrons on tracks certainly do little for the "why" of the covalent bond and are useless in discussing molecular shapes and properties. Electrons stationary at the corners of tetrahedra or cubes should bother any student with a grasp of elementary physics, since this picture violates classical physics as badly as does the quantum theory.

A really fundamental discussion of atomic electrons might start with the eigenfunction for the ground state of the hydrogen atom:

$$\psi_{1s} = Ne^{-r/a_0} \qquad (1)$$

However, the prudent instructor in freshman chemistry will delay any such introduction, at least until after the deadline for dropping the course.[1] This equation has only one symbol (r) which the average student may readily understand. As a starting point it is not highly satisfactory. To discuss atomic and molecular orbitals with undergraduate students, pictures and models are required.[2] A dynamic method of representing the combination of simple atomic orbitals to form hybrid and molecular orbitals is the subject of this paper. Projected images of simple orbitals (Fig. 1) may be combined in a variety of ways to illustrate various concepts of modern molecular theory (Fig. 2).

Projection of Simple Orbitals

Orbitals are often represented by pictures shaded to represent the gradual variation of electron probability. These fuzzy pictures may remind one of photographs or projections horribly out of focus. The 1*s*, 2*s*, and 2*p* orbitals in Figure 1 were made indefinite in just this way—projected images of the various orbitals were made fuzzy by using the projector out of focus. The defocusing may be said to correspond to the introduction of the uncertainty principle for the purpose of elementary discussion, but the analogy had perhaps best not be pushed too far.

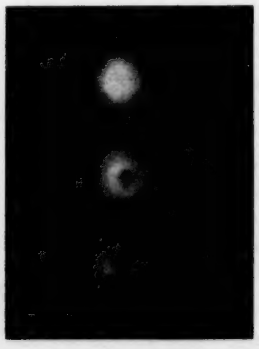

Figure 1. Projected images of simple atomic orbitals. Top: 1*s* in hydrogen. Middle: 2*s* in carbon. Bottom: 2*p* in carbon.

The scheme for producing the images photographed in Figure 1 is shown in Figure 3. An overhead or overcast type projector is equipped with two Polaroid sheets P and P′; these are crossed so as to black out the screen. Orbital models (M and M′) may then be made from any optically active material and introduced between the Polaroids. Bright images of the orbitals will be produced on the screen. Thin cellulose acetate sheets are very suitable for the orbital models. Areas of high electron probability may be made brighter by superimposing two or more layers. The images of Figure 1 were produced by such superimposed orbital models, cut as shown by the contour maps of Figures 4 and 5. The sharp contour-line edges of the various pieces disappear as the projector is defocused. The contour edges represent, of course, definite amplitude values of the atomic-orbital eigenfunctions.[3]

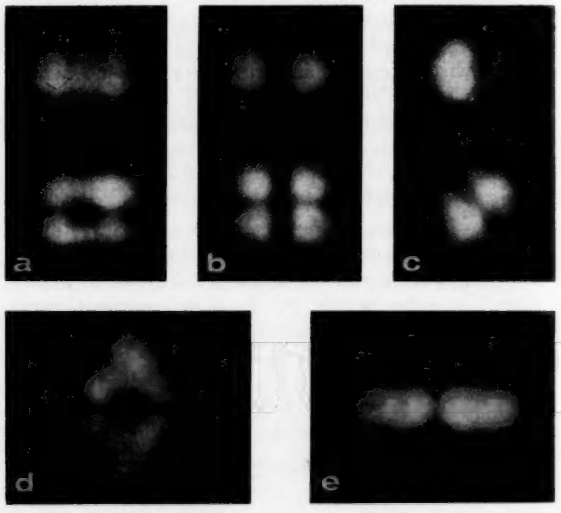

Figure 2. Orbital combinations. a, bonding orbitals; top, σ_{1s} as in H_2; bottom, π_{2p} as in C–C double bond. b, antibonding orbitals σ_{1s}^* and π_{2p}^*. c, atomic hybrids; top, *sp*; bottom, diagonal *p* orbital formed from horizontal and vertical *p* orbitals. d, protonated double bond. e, σ_u orbital in MH_2-type molecule.

[1] As noted by Dr. J. G. Calvert during the discussion of this paper, equation 1 may well be represented to freshmen, with proper discussion and illustration.

[2] Models of various types have been worked out. See WISWESSER, W. J., J. CHEM. EDUC., **22**, 314 (1945) and LAMBERT, F. J., J. CHEM. EDUC., **34**, 217 (1957).

[3] A number of articles on modern atomic and molecular theory have appeared in THIS JOURNAL. See for example NOLLER, C. R., **27**, 504 (1950); CAMPBELL, J. A., **25**, 558 (1948); KIEFFER, W. F., **25**, 537 (1948); WISWESSER, W. J., **22**, 314, 370, 418 (1945).

Presented in part before the Division of Chemical Education at the 133rd Meeting of the American Chemical Society, April, 1958, San Francisco, California.

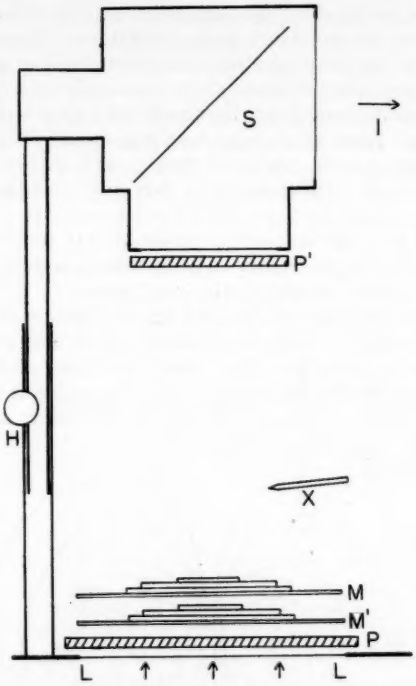

Figure 3. Overhead projector arranged for orbital projection. *L*, light from source; *P*, *P'*, polaroid sheets; *S*, lens and mirror system; *I*, direction of screen; *H*, height (focus) adjustment; *X*, position of pointer (in focus).

Cellulose acetate sheet is an anisotropic solid with optical axes parallel to the edges. The anisotropy is undoubtedly due to molecular alignments produced in the manufacturing process. Accordingly the optical axes will be parallel to the edges of the sheets as manufactured. Smaller sheets are usually cut in the same directions. This leads to elliptically polarized light, complicating somewhat the analysis of the resulting images. For our purposes it suffices to note that bright images are produced from pieces of cellulose acetate sheet so long as the optical axes of these pieces are not parallel to those of the crossed Polaroids. Further, if two pieces are placed with a given optical axis rotated in equal and opposite directions from an axis of the Polaroids, a cancellation is achieved and areas where the two pieces overlap will appear dark. This latter effect is of importance in producing orbital combinations.

Orbital Combinations

Two important concepts in modern molecular theory involve combinations of simple atomic orbitals: molecular orbitals and hybrid atomic orbitals. The models described above may be overlapped to represent both ideas. Figure 2*a* (top) shows the result of bringing together two 1*s* orbitals. The resultant is the σ_{1s} molecular orbital used to discuss the structures of the hydrogen molecule and molecule-ion. Two 2*s* orbitals may be similarly combined. Two 2*p* orbitals may be brought together end-to-end to form a σ_{2p} orbital or side-to-side (overlapping both lobes) to form the π_{2p} "double bond" orbital shown in Figure 2*a* (bottom). These combinations may be made before the students, by moving the orbital models in the field of the projector. The building up of "electron density" between atoms as they come together is made very evident in this manner.

As noted previously, opposite orientations of the cellulose acetate pieces lead to cancellation of the image. Thus the two orientations can represent opposite signs of the wave function. By appropriately reversing or rotating the orbitals the anti-bonding combinations may be produced. Figure 2*b* shows σ_{1s}^* and π_{2p}^* anti-bonding orbitals. These may be made before the observer by merely reorienting the orbitals used to make the combinations in Figure 2*a*. The vertical dark nodal planes which separate the atoms appear dramatically as the simple orbitals are pushed together.

Figure 2*c* shows an *sp* atomic hybrid formed by superimposing a 2*s* upon a 2*p* orbital. The component orbitals add at left and subtract at right, illustrating the highly directional nature of the hybrid. The other *sp* hybrid may be shown by rotating the upper (2*s*) model. The second *sp* hybrid is correctly oriented at 180° to the first. Rotation of the 2*s* orbital model corresponds to varying the magnitude and sign of the *s* contribution to the hybrid. Thus the effect of change in *s*-character in the series *sp*, sp^2, sp^3, *p* may be shown.

Overlaying two 2*p* orbitals oriented at 90° results in a *p* orbital at 45° to each parent. Reversing the sign of either parent will produce another *p* orbital at 90° to the first "daughter." These combinations (Figure 2*c*, bottom) of members of the degenerate set of *p* orbitals thus correspond to a change in orientation only.

Combinations of three or more atomic orbitals are employed in more advanced discussions. For example, an early discussion of the bridge hydrogens in diborane involved "protonated double bonds."[4] Figure 2*d* shows a projection of this idea. The *p* orbitals of the two boron atoms are oriented as for π bond formation, and hydrogen 1*s* orbitals are added above and below. The pencil pointer indicates the position of one boron nucleus. The pointer is kept in sharp focus by holding it in the focal plane of the projector, somewhat above the orbital models. (See also Figure 3.) Three-center bonds, used in more recent treatments of the boranes,[5] may also be shown.

Figure 2*e* shows an orbital used by Walsh[6] in discussing shapes of molecules of the type AH_2. This σ_u orbital is made by appropriate combination of 1*s* orbitals on the hydrogens with a 2*p* orbital on the central atom. The other bonding, anti-bonding, and non-bonding orbitals of this discussion may be produced similarly.

Further Possibilities

The variety of combinations of three simple atomic orbitals described above illustrates the versatility of this way of showing the linear combination of atomic orbitals. Numerous improvements will no doubt occur to readers. Atomic orbitals of differing sizes would illustrate hetero-nuclear polar bonds. Single piece sp^2

[4] Pitzer, K. S., *J. Am. Chem. Soc.*, **67**, 1126 (1945).

[5] See, for example, Lipscomb, W. N., *J. Chem. Phys.*, **27**, 212 (1957).

[6] Walsh, A. D., *J. Chem. Soc.*, **1953**, 2260, 2266, 2288, 2296, 2301, 2306, 2321.

and sp^3 models would be convenient in discussing localized molecular orbitals in many molecules. However, the simple orbitals and techniques described seem sufficient for undergraduate introductory and physical chemistry.

Theoretical and Technical Details

Theory. Light-wave amplitude is in this process the analogue of the amplitude of the wave function, so that light intensity is the analogue of the probability function ψ. In forming combinations the individual light amplitudes are added rather than the intensities. The covalent bond representation thus corresponds to simple molecular orbital theory. In forming a σ_{1s} orbital, for instance, overlapping between the 1*s* atomic orbitals doubles the light amplitude, quadrupling the intensity.

For small angles between the optic axes of Polaroids and models, transmitted light amplitude is a nearly linear function of the number of layers of plastic employed. However, the best visual results seemed to be obtained using contours $\psi = 0.05$, 0.1, 0.2, and 0.3. The largest error, in theory, is that defocusing the projector produces the same fuzziness in all regions, while some portions of the actual wave functions have high gradients, and the images should be correspondingly better defined in these areas.

The functions used are Slater's approximations[7] for 1*s* in the hydrogen atom, 2*s* and 2*p* in carbon. Accordingly, the functions employed are

$$\psi_{1s} = 0.32\, e^{-r}$$
$$\psi_{2s} = 1.1 \times e^{-1.625r}$$
$$\psi_{2p} = 1.0 \times e^{-1.625r}$$

While these functions are normalized and therefore may fairly be compared one with another, the resulting combinations are not. However, the viewer compares each region of the image with other regions before him rather than with what he saw a few moments ago, thus supplying a sort of psychological normalization.

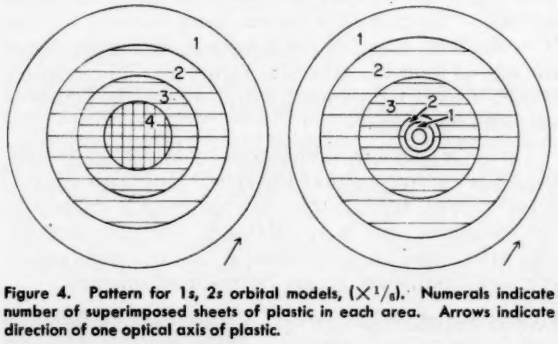

Figure 4. Pattern for 1*s*, 2*s* orbital models, ($\times 1/6$). Numerals indicate number of superimposed sheets of plastic in each area. Arrows indicate direction of one optical axis of plastic.

Construction of Models. The orbital models are made by cutting appropriate pieces from 0.003 in. cellulose acetate sheet. The pieces required are shown in Figures 4 and 5. All the exercises described may be performed using two orbitals of each type. The arrows show the direction of an optical axis of the plastic. The pieces should be cut with all the arrows parallel to the same edge of the sheet. Be sure not to reverse or turn the pieces before mounting.

[7] SLATER, J. C., *Phys. Rev.*, **36**, 57 (1930).

The sheet used by the author was sold by the college bookstore for notebook page protectors. Five or six layers of this may be superimposed without producing undesirable color effects. Cellophane will not work.

The orbital models are best mounted on a transparent backing. Glass sheets have been suggested. The backing sheets must be isotropic, apparently ruling out most plastic sheet. However, 8- × 8-in. pieces of the same plastic as used for the orbitals will serve if two layers are cut and the second is turned at 90° to the first. The two large pieces may be placed above and below the orbital models, protecting the small pieces.

Holding models and backing sheets together presents some problem. Most transparent glues and cements dissolve or otherwise affect the plastic and thus show up on the projected images. An alternative is to staple the pieces in place. As soon as the image is defocused the staple disappears.

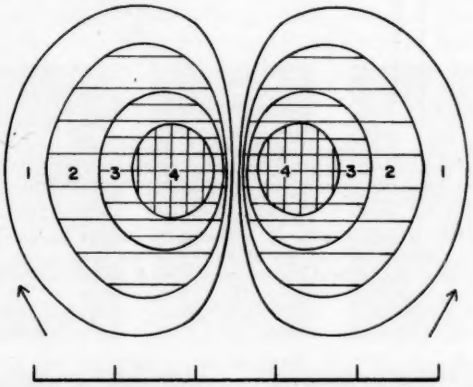

Figure 5. Pattern for 2*p* orbital model. ($\times 1/2$). Scale at bottom is in Bohr radii: one unit = 0.53×10^{-8} cm.

Care should be taken to align each piece of each orbital as shown in Figures 4 and 5. So that the proper orientation of each orbital for the desired combinations can be found easily, the 8- × 8-in. finished unit should be identified in a given corner. Conveniently, the orbital designation (1*s*, 2*s*, 2*p*) may be printed in the lower left with India ink.

Projection Procedure. First the Polaroid sheets must be mounted on the projector (see Fig. 3). The lower sheet P may be laid to cover the 10- × 10-in. light opening. Two pieces of adhesive tape will help hold it in place if desired. The upper piece P′ is most conveniently a circle, cut to fit inside the opening of the lens system. In this position it may be held by some sort of snap ring. Alternatively, P′ may be a smaller sheet mounted over the lens opening and held in place with adhesive tape. In either case, the two pieces must be crossed; that is, P′ must be rotated until the entire screen is dark.

Any one of the orbital models may now be laid over P with its edges parallel to those of the Polaroid. An image will appear on the screen. With the project in focus, the inner (three- or four-layer) areas should appear brightest, successive contours appearing darker as one progresses outward. If each model does not have this appearance, some mistake was made in mounting the individual pieces. Rotating the model varies the light intensity; the models should commonly be used with their edges parallel to the edges of P. A ruler

taped in place parallel to an edge of P is sometimes helpful in keeping the models lined up.

Finally one must defocus the projector until the contour edges are obscured and the entire image has the desired appearance. The only difficulty in obtaining the desired orbital combinations should be finding the proper relative orientations for the models. For this purpose it is important to practice before using.

Acknowledgment

Oliver Hagglund served as adviser on projection techniques for this project. The author is grateful to Mr. Hagglund and the Audio-Visual Department of Gustavus Adolphus College for help and advice, and for the use of projection and photographic equipment.

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Research Programs for Undergraduates

Research has been defined as a "way of thinking," a way, that is, which presents something new to a student above and beyond textbook material and which challenges him to independent thinking. What he accomplishes may or may not be publishable, but this is incidental. The term, "original research," however, does indicate publishable work. It may be a study of laboratory technique, theory, or even a review of past accomplishments in the field of science (*1*). In chemistry the research approach to teaching has been introduced at many colleges and universities on curricular levels ranging from the special qualitative unknowns (*2*) and the open-end experiments (*3*) of the freshman year on through to the senior thesis. But whatever the level the problem should be so skillfully chosen that the student's curiosity is aroused within the framework of fundamental chemical knowledge. Caution, however, must be maintained: the research approach is so stimulating to the better student that his enthusiasm may be considered both by the professor and the student as proper justification for a course which does not cover the requisite fundamentals of chemistry. Research as a "way of thinking," then, implies thoroughness of background attained by the solution of skillfully worded problems rather than by conventional laboratory and recitation assignments. Less frequently encountered at the undergraduate level are programs of original research involving both student and professor (*4*).

A few professors in undergraduate colleges working independently have maintained an excellent record of publication, but most programs of original research involving an appreciable number of undergraduate students are of fairly recent origin. These have been made possible by support from foundations which have recognized the liberal arts college as representing a relatively untapped source of research information. Probably of even greater significance is the recognition by these foundations of the important role of undergraduate research in attracting students to chemistry and encouraging them to continue their education in graduate school. In a university where the graduate research program creates an atmosphere conducive to original work, the problems are different from those in the liberal arts college where research in chemistry may represent the only original research on the campus.

At both the college and the university original research programs vary from those supporting, on a small grant, the work of a single student during the school year to contract research which requires the active participation of several professors and many students for eleven months each year. Recent grants from the National Science Foundation (*5*) have increased student participation in active research programs and have encouraged many colleges to begin such programs in chemistry and in other sciences. In this atmosphere of heightened interest in undergraduate research a consideration of the important features of successful programs may be pertinent.

Many began with a small grant from the Research Corporation which paid a salary to one or two students assistants and supplied a modest amount for supplies and equipment. The professor did not receive additional salary. From this beginning, programs involving three or four professors, many students, and large budgets have developed.

Undergraduate Research: Problems and Policies

As an undergraduate program grows, many problems beyond the statement and solution of the research "problem" are encountered and the success or failure of a program may depend upon their proper solution. These problems will be discussed on the bases of thirteen years of active participation in undergraduate research at Grinnell College and of informal discussions at the Wooster Conference (*6*) with men who have been similarly engaged.

The problems can be divided into several categories. There are those broad and important ones which consider and evaluate the role which undergraduate research should play in the national research effort and

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those that are concerned with the relation of the program to the educational objectives of the college. A complete solution to these problems can never be achieved, but careful consideration of each is important.

At one extreme, undergraduate research has been considered as a useful device for the investigation of minor problems (*7*); at the other, as a device for really important exploratory work in the borderline areas between the sciences (*8*). This latter suggestion has a bearing on the future of undergraduate research and the national research effort in general. Its amplification and expansion are important.

Research in the graduate schools frequently involves a candidate for a degree and requires that positive results be obtained for a satisfactory thesis. The problem normally begins within a framework of well-defined information and proceeds to its solution by way of standard techniques. Excellent research is accomplished by this procedure, and is, in large measure, responsible for the present eminent position of science. Professors at undergraduate colleges are usually products of this system and normally continue their research in a similar manner. This is probably the easiest way to obtain adequate and continuing support for a project and to compile a record of publication, since the results are tangible and often impressive. On the other hand, it ignores the accusation that research in the United States, excellent as it is, does not uncover new concepts and areas for study to the same extent as in certain other countries. Research in the undergraduate colleges where it is not burdened by the requirements of positive results or the pressures for publication should be effectively channeled into the investigation of new areas where even the procedural techniques may be ambiguous. It is encouraging to know that a start has been made. A conference has been held at Defiance, Ohio, to consider the role of the liberal arts college in research in the borderline areas between the sciences (*7*). It appears to me that the undergraduate college can make its most important contribution to the national research effort by deliberately directing its research into these less well-defined areas. Whether these are borderline between the sciences or fall entirely within a single science seems relatively unimportant.

The objectives of an undergraduate research program are more easily defined than the role of undergraduate research in the national research effort. In the liberal arts college the primary objective must be the effective training of the student. In achieving this objective the program should attract the better students to the study of chemistry; it should make their work in chemistry more stimulating, and it should encourage them to continue their study in graduate school. A secondary objective is, of course, publication.

Publication of good research papers brings prestige to the student, the professor, the department, and the college, but publication should always remain less important than the training aspects of the program.

The Problem of Support

Now that the role of research in the national effort and the objectives of research have been examined, several questions must be considered: What foundations are most likely to support research in a liberal arts college? What types of grants are available? How are grants obtained? What items of the budget are necessary and on what bases are these items justified?

Many foundations have shown an interest in undergraduate work: fifteen sent representatives to the Wooster Conference to present their programs and to consider how they might be useful. The foundations which appear to be the most likely sources of funds for undergraduate research are the National Science Foundation, the Petroleum Research Fund, and Research Corporation, although support has been obtained in special circumstances from many other foundations and agencies. Direct financing of undergraduate research by industry is uncommon, but indirect support may occur by using portions of industrial grants such as those of the DuPont Company or of Standard Oil.

The types of support available from three foundations active at the undergraduate level can be briefly summarized. The National Science Foundation, which provides the greatest amount of support, has two types of grants particularly useful to an undergraduate research program.

The first type is similar to the grants available to graduate schools. It provides salary for the professor and his students, an allotment for supplies, equipment, travel, and stenographic expenses. Fifteen per cent of the grant is permitted as overhead to the college. This grant is awarded only after an evaluation of the research proposal and a consideration of how efficiently it may be carried out. Since there is never enough money for all requests, these proposals are in keen competition. Approval is certainly not automatic. The National Science Foundation also has a relatively new type of grant directed specifically to the undergraduate research program. It provides salaries for students, limited funds for equipment and supplies, and some overhead for the college. In this type of grant the interest of the Foundation lies more in the training aspects of the program than in the research output although, of course, there is effort made to encourage worthwhile projects.

The Petroleum Research Fund has recently introduced its Type B grants (*9*) to professors at undergraduate colleges. On May 1, 1959, thirty-six grants averaging $3720 each were in effect. These grants permit salary, overhead, and equipment, the usual expenditures allowed by the research grants of the National Science Foundation. They are similar in that they require a minimum of red tape and reporting.

The Research Corporation has been and continues to be a most useful source of support for the professor in a small college who wishes to start a research program. A Research Corporation grant does not normally pay salary to a professor or overhead to the college, but it does allow salary for students and expenditures for equipment and supplies.

Each of these foundations has a brochure describing exactly what a professor should do to have his research proposal evaluated. Grants which do not pay salary to the professor can usually be obtained by submitting a simple statement of the research problem and a brief

outline of expenditures. For grants involving salary for the professor and the more extensive budgets, competition makes it imperative that the proposal state the research problem clearly, with emphasis upon both its practical and its theoretical importance.

In addition to a clear statement of the problem, it is necessary to include a statement of the expenditures necessary for carrying out the research. Salary for the professor, salary for the students, an allotment for supplies and equipment, travel, stenographic assistance, and overhead must be budgeted. A decision must be made regarding the amount requested for each of these items. Some of the decisions which have been made at Grinnell College may be helpful to others facing similar problems.

It is easy to decide upon the salary which should be requested for two months of work during the summer, since this has been set by the foundations as two-ninths of the professor's annual pay. Regardless of the number of grants he may receive, we believe that a professor should not receive a research salary that exceeds this stipulated sum. An adequate research salary, however, usually assures the professional attention of the professor to his program, and this goes a long way toward making his program a success.

The salary level for student assistants is another problem. Many chemistry students must earn money to pay for all or a part of their education and they are capable of obtaining industrial work during the summer at high wages. At the same time student wages on the college campus may be inadequate. At Grinnell, we have split the difference between the college and the industrial rate. We pay at the hourly rate of $1.25 for inexperienced students and $1.50 for those with experience. At these rates the expenditure for the average student is about $600 for the summer and $150 for the academic year.

A decision regarding the amount for supplies and equipment depends, of course, upon the demands of the research problem. When no unusual and expensive equipment is needed, we have found that an annual expenditure for supplies and equipment will average between $200 and $300 per student. A round figure of $1000, then, will supply a student with research facilities and pay his salary. This estimate assumes that the facilities of the department are available for research.

Attendance at meetings is essential if a professor is to present the results of his work and keep abreast of current developments in his field. At Grinnell College each professor's expenses for travel have averaged about $250 per year. This amount permits attendance at only a single meeting, if great distances are involved. When meetings are close to home, it is possible for the professor to attend several and also to subsidize the attendance of his research students as well. There are many miscellaneous stenographic expenses: research grants require research reports, and continued income requires renewal requests; publication requires typed copies of an original paper, and reprints are necessary; slides are required for presentations at meetings. To the extent that the college does not provide for these miscellaneous stenographic expenses, the research grant must do so. The portion of the Grinnell program involving one professor and five students pays out an average of $200 per year for these services.

Because they believe that a college should subsidize the research of its faculty, some foundations have been reluctant to allow overhead in their research grants. While it is true that a good college should support the research of its faculty, this certainly does not mean that this support should arise from uncontrolled subsidy of research grants. A single research project by a professor and several students may not be expensive, but when this project grows to a program involving many professors and many students in several departments of the college the cost does become significant. It is difficult to determine the actual cost of a program. Our business office has accepted fifteen per cent of each grant as a reasonable estimate. It is the obligation of each professor to include in his proposal the amount of overhead which his college believes to be necessary.

Responsibilities of the Professor

Even after funds have been made available and the objectives of the research established, there remain still other responsibilities for the research professor, responsibilities which involve students and other departments. A proper awareness of these is essential for a successful and harmonious program. They include selling the program to the students, hiring and housing them, seeing that recreational facilities are available, introducing accepted safety procedures, and finally adapting the research for salary to the college program of research for credit.

One of my former students posited the need for selling a research program by asking me, "Why should I do research for $1.25 an hour when I can make $2.00 on the construction crew?" Our decision not to compete with industrial salaries means that the program must be sold to the student on a basis other than that of the money he will earn. This is probably a good thing because it keeps the professor aware of his obligation to the student. Selling a program is best achieved through the enthusiasm of students who are already in the program, the obvious dedication of the professor to his research, and his honest conviction of its importance. It is more effective to attract students to the important work which needs doing than to emphasize the value of the research experience.

Before hiring students we post a list of research positions with a brief description of each one, and the student applies for the position which interests him by listing his qualifications and stating his reasons for wishing to do research. Although preference is given to students with advanced standing, a promising freshman is not shut out. This formal procedure acquaints all students with the research of the department and encourages them to apply for a position. When they are chosen, they seem to consider it an honor.

While housing and recreation are not the direct obligation of the professor, they have an important effect on morale. During the summer Grinnell College has provided a section of one of its dormitories for men students; women students have taken over one of the faculty homes. In the early stages of our program one or two men students, staying for the summer in a small college town, found living rather dull, and attempts by

the professor to relieve their boredom were unsuccessful. Last summer, with their number increased to ten students in chemistry, eight in biology, and four in physics, they made their own recreation. Probably as important as the increased number of students in improving the recreational aspects of the program was the participation of four girls. A program involving eight or more students appears to me to create its own social life. This is particularly true when several of the students are women.

It would be gratifying to believe that a happy student is a careful student, but this is not so. Even after the best safety practices have been followed, most professors of chemistry are both relieved and thankful when another year has passed without a serious accident. Undergraduate research requires special emphasis on safety since young and inexperienced students are always involved. We certainly do not have an answer to the safety problem but we do have a policy.

Research students are informed of the importance of safety when they enter the program, and this importance is re-emphasized at the beginning of each summer. Students are permitted to work six days each week between the hours of 7 A.M. and 6 P.M. with at least one other student within calling distance. No one works alone. Even though students are hired by and work for the professor, the business office of the college arranges that they be insured against accidents as employees of the college.

A university may have a man or a department responsible for distributing and accounting for research funds. Since the business office of a college rarely provides this service, each professor should be responsible for the accounting and distributing of his own grants. After considerable difficulty between research professors and our business office, we have now worked out a satisfactory arrangement. The business office introduces a separate account for each research grant and insists that each invoice designate the account to which it must be charged. A complete record of income and expenditures for each grant is available in the business office. In addition to these records each professor maintains an account of his income and expenditures for each of his grants and assumes full responsibility for following the rules of the grant. This, of course, is a simple and obvious procedure. It is mentioned only to emphasize the fact that in a liberal arts college, as much as he might wish it otherwise, the professor himself must assume full responsibility for the administration of his grants.

A successful research program with pay for students is not automatically integrated with the program of research for college credit. Should a student be paid for work for which he receives college credit? At Grinnell College we have decided that undergraduate students should not receive pay and credit for the same work. This decision was made to eliminate the advantage that a department offering both for the same work might have over a department offering only credit. During the academic year, it is an unusual student who can maintain a weekly average of ten clock hours in research for credit. Thus about 300 hours divided into small segments can be devoted to a senior research project. This may be anticlimactic for the student who has worked eight or ten hours a day on research for several summers. We have found it effective to arrange our research program so that students will work on their own research projects, leading to their senior theses, during the summer preceding their senior year. Their pay is discontinued at the beginning of the academic year but their laboratory work continues through most of the first semester. Thus the entire second semester can be devoted to the correlation of data and the writing of the thesis. By this arrangement the work for credit is satisfactorily integrated with the professional research program.

No Substitute for Enthusiasm

Even after all of these problems and questions have been satisfactorily disposed of, a research program will not necessarily be successful. The heart of a successful program is the efficiency and enthusiasm which a professor shares with his students. Except for subdivision of the work into smaller segments and more supervision, a successful undergraduate program does not differ materially from a graduate program. However, because of the inexperienced workers and the segmented nature of the research, it is imperative that each student understand and appreciate not only the long range objectives of the research but the contribution his own work will make toward achieving these objectives. The undiminished and sincere interest of the professor will aid him greatly in keeping this perspective. The program should have always before it really important theoretical goals. Teaching is involved in a student's understanding these goals and in the excitement engendered by his being a part of important work. Of course every research student will develop new laboratory techniques and be introduced to large amounts of new knowledge, but what is most important is that each student should understand his specific problem and the part that it plays in the over-all achievement of the research project. It is only in this way that he can contribute creatively. A student will gladly become a pair of hands for the professor. Some of them will even work long hours with a dedication leading to the exclusion of important undergraduate activities. What a student must be led to develop might be called professional maturity. It is not directly related either to long hours of work or to laboratory skills, but depends upon the student's acceptance of his piece of research as his own responsibility. When he does this, he will insist upon a clear statement of his problem; he will read the literature bearing upon it; he will ask questions and suggest new approaches. All students certainly do not achieve this professional maturity, but being a part of an efficient and well-organized program certainly gives them the opportunity.

There are a number of devices which help a student understand his research and encourage him to assume professional responsibilities. One of these is his presentation of a paper at a state academy, a regional student research symposium, or even a department seminar. Both the students presenting papers and other students as well seem to be impressed. Another device which has been an important feature of the Grinnell program for several years is this: every Friday afternoon all research students participate in a research meeting. Each student describes his own problem and

its relation to the broad research objectives, tells what he has accomplished during the week, and outlines what he hopes to accomplish during the coming one. Speeches are limited to fifteen minutes and critical discussions follow. These sessions keep each student aware of all of the research in the department and make him evaluate his own work at frequent intervals. Written progress reports and a final report are also required. Near the close of the summer a formal research meeting is held at which students present formal papers. Mimeographed abstracts, luncheon, and invited guests simulate the one day meeting which has been so effectively used by local sections of the American Chemical Society. Although these reports and meetings may reduce the time spent in laboratory research, they are valuable in their own way as they serve as stimuli to the student's understanding of his problem and to his acceptance of professional responsibility.

Some of the factors which contribute to the success of an undergraduate research program have been mentioned and discussed, but the subject is by no means exhausted. Different students, different professors, different programs will encounter their own problems and create their own solutions.

While original research is an efficient method for training chemists, the excellent record of many professors having no publications beyong their doctoral thesis clearly demonstrates that it is not the only method (*10*).

The rewards of the undergraduate research program are indeed twofold. The student learns self-reliance and develops an appreciation of research. For the professor who is his mentor and who faithfully works on campus eleven months a year a different reward is assured. As students whom he has trained make their tremendous or even their modest contributions to science he can claim them as "his men."

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Chem Gems

Physical and organic chemists have been carrying out good-natured feuds at least since the days of Ostwald and Liebig. Thus were the following news items to appear in a local newspaper or periodical the reactions would be as follows: The first would confirm the worst suspicious of many organic chemists whereas few physical chemists would doubt the veracity of the second.

NEWS ITEM—Modern electronic magic has scored another major advance in the high-speed computational field. As is well known, the success or failure of physical chemical research depends on the nature of the graph resulting from the plot of one variable as a function of another, everything else except blood pressure held constant. If a curved line results progress is being made; a straight line portends the evolution of a new theory, and if the line goes through the origin—EUREKA. Previously, the only known sure-fire method of making the transition from progress to the Nobel prize was to introduce impurities to the system and keep plotting. No more, announces a spokesman for the Inter and National Burgeoning Machines Corporation. INBM's new, inexpensive, stadium-sized desk digital computer, the Snark IV–SLOB (Straight Line Origin Bender) makes it possible to obtain a linear plot of any two variables which go through the origin. According to the INBM spokesman, it is not even necessary to hold anything constant unless purely theoretical results are desired. Furthermore, the introduction of impurities is unnecessary. Results are printed out by an ultra-high-speed electric typewriter on standard Scotch tape which can then be stored on blank wall spaces or used to hold up office periodic tables. A not-to-be-minimized advantage of this latter innovation lies in the release of valuable filing cabinet space for inter-departmental directives, picnic announcements, red tape, lunch boxes, and back issues of . . . magazines. The upshot of the new development is that now every physical chemist can publish a paper with a linear plot regardless of the difficulty of his specialty. This should not only make it easier to make editorial decisions regarding prospective papers but will contribute toward greater uniformity of articles as well.

NEWS ITEM—One of the problems confronting those who teach courses in organic chemistry concerns the excessive number of hours necessary for completion of the laboratory requirements of the course. In a normal five-credit, one-semester course students must spend around eight hours per week in order to carry out the required syntheses. Now all those long, grueling hours of watching reflux condensers are gone forever, says Dr. H. Jethro Knave of Pugwash University. Exhaustive experiments carried out at PU over the last several years indicate that laboratory time can be reduced by as much as 75% by the simple expedient of providing laboratory manuals with waxed pages. Dr. Knaves points out that the waxed page cuts down on frictional losses involved while the student runs his finger along the page in search for the ingredient to be added next. Dr. Knave states that the idea occurred to him when he accidentally picked up a physical chemistry text in the library and spotted a paragraph on frictional forces. "Naturally," said Dr. Knave, "since I am an organic chemist I had never heard of friction before." Asked by reporters to comment on the significance of his discovery, Dr. Knave would only say that he regarded it merely as another triumph of the discipline of organic chemistry.

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Conformational Analysis in Mobile Systems

By "conformations" of a given molecule are meant the infinite number of arrangements produced by rotation about single bonds. Since such rotation is not free (*1*), and since some of the rotational arrangements are appreciably more stable than others, a given molecule will spend most of its time in one or other of a few "stable conformations." For example ethane (Fig. 1) normally exists in one of three identical conformations in which the hydrogen atoms are "staggered" and which correspond to potential minima with respect to rotation about the carbon-carbon bond.[1] These potential minima or valleys are separated by potential maxima or hills called "energy barriers." In the case of ethane, the potential maxima correspond to conformations in which the hydrogen atoms are on top of each other—so-called "eclipsed conformations" (Fig. 1). The reason why the potential energy of the eclipsed conformation exceeds that of the staggered conformation by almost 3 kcal/mole is still controversial (*2*) but the experimental fact is established beyond doubt.

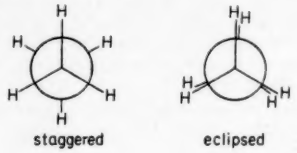


Figure 1. Ethane.

Butane (Fig. 2) may exist in three different stable conformations, sometimes called "conformational isomers" or "conformers," namely the stable "*trans*" or "*anti*" conformation[2] and two mirror-image metastable "*gauche*" or skew conformations. These, in turn, are separated by energy barriers of 3–7 kcal/mole corresponding to eclipsed conformations.

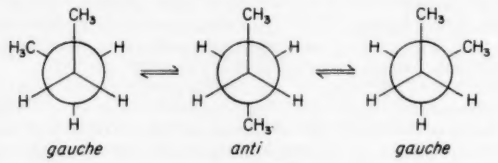


Figure 2. Butane.

A monosubstituted cyclohexane may exist in two chair conformations (Fig. 3) which may be interconverted by flipping up one side of the chair and flipping down the other. This transformation proceeds via a flexible (boatlike) form and involves an energy barrier of less than 10 kcal/mole.

Figure 3. Monosubstituted cyclohexane.

The reader who is not familiar with conformational problems should construct a ball-and-stick model of cyclohexane at this point. A large number of interesting facts may be inferred by careful inspection and manipulation of the model, for example: (1) In the chair form, all carbon-hydrogen bonds are perfectly staggered (this is why the chair is the stable conformation). (2) There are two types of bonds in the chair—three pointing up and three pointing down (which are called "axial bonds") and six pointing outward (which are called "equatorial bonds"). Substituents attached to axial bonds if larger than hydrogen are closer to each other than corresponding substituents on equatorial bonds, and therefore a substituent in the axial position (Fig. 3(A)) is more encumbered and less stable than a substituent in the equatorial position (Fig. 3 (E)). (3) There are two chair conformations; one may be transformed into the other with some effort by bending down the back and bending up the front feet of the chair. In the process, all substituents which were originally equatorial become axial and all substituents originally axial become equatorial (this is best seen by using balls of different color for the axial and equatorial substituents in the orginal chair). (4) The intermediate in the transformation of one chair into another appears to be a boat-shaped form. This form has several unfavorable interactions, notably two pairs of eclipsed hydrogens (*cf.* Fig. 1) on each side and another pair of hydrogens (at the "bowsprit" and "flagpole") which interfere with each other sterically. It will also be seen, however, that the model of the boat is quite mobile; a few manipulations will convert one boat into a second one and that one into yet a third, etc. In the process of transforming one boat into another, one passes through an intermediate form in which neither the eclipsing of the hydrogens at the side nor the "bowsprit-flagpole interaction" is as severe as in either of the two boats. This form is called the "flexible form," and it, rather than a true boat, is probably the intermediate between two chairs which are being interconverted. For further details, see ref. (*10*).

By "Conformational Analysis" is meant the analysis of the physical properties and chemical behavior of a molecule in terms of the geometry and population of

The material for this article is taken in part from three lectures delivered at the Conference on Chemical Bonding at Tufts University, July, 1959. This Conference was made possible by a grant from the National Science Foundation.

[1] Regarding the notation used here, *cf.* NEWMAN, M. S., J. CHEM. EDUC., **32**, 344 (1955).

[2] Heretofore, this conformation has always been called "*trans*," but this designation has given rise to much confusion, since the term "*trans*" is also used to denote configuration in disubstituted ethylenes and cycloalkanes. The two conflicting meanings are by no means coextensive: thus two adjacent equatorial substituents in a rigid cyclohexane system (e. g., decalin, Fig. 4) are configurationally *trans*, but conformationally *gauche*. This confusion is avoided by using the term "*anti*" for diaxial or antiparallel groups and reserving *trans* for configurational nomenclature. (Confusion with the use of "*anti*" in the configurational designation of oximes is not likely to arise.)

various conformations in which it may exist. A number of excellent reviews of the subject are available (*3–10*). Although the existence of several conformations of substituted cyclohexanes was recognized by Sachse almost 70 years ago (*11*), and the existence of energy minima in aliphatic hydrocarbons has been known for almost 25 years (*1*), it was not until after the appearance of a pioneering paper by D. H. R. Barton (*12*) that chemists in general began to understand the importance of conformation in assessing chemical reactivity.[3]

Mobile Systems

Most of the early examples (*12*) regarding stability and reactivity of equatorially[3] and axially[3] substituted cyclohexanes are concerned with compounds whose conformation is unequivocally determined, either because the molecules are rigid, such as substituted *trans*-decalin (Fig. 4) and ring systems (such as steroids, polycyclic terpenes, etc.) derived from *trans*-decalin, or because of the two possible conformations of the molecules, one involves an excessive number of unfavorable axial interactions, such as menthol (Fig. 5).[4]

Figure 4. *trans*-Decalin.

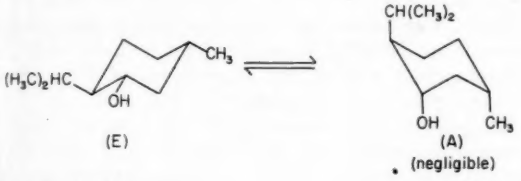


Figure 5. Menthol.

Nevertheless, most simple cyclohexane systems, such as monosubstituted cyclohexanes (Fig. 3), may exist in two conformations which are in equilibrium with each other, which are separated by a relatively low energy barrier, and both of which exist in appreciable proportion at equilibrium. If one looks at a chemical reaction of such systems, one really has to look at the reaction of both conformational isomers, as depicted in Fig. 6. The kinetics of such a reaction was worked out independently by Winstein and Holness (*13*) and in our laboratories (*14*) and is as follows:

[3] If the reader is not familiar with the basis of conformational analysis, it is strongly suggested to him that, rather than continue reading the present article, he turn to one of the reviews for background information at this point. Ref. (*10*) is particularly recommended for this purpose, since it is fairly up-to-date and contains much basic material. Ref. (*9*) which summarizes many fascinating consequences of a conformational analysis of cyclohexane chemistry is strongly recommended to those who have some basic background information. Even if the reader, after reading the above reviews, does not find the time to return to the present article, the author feels that he has performed a worthwhile service by attracting the reader to this important field.

[4] The reader should construct a ball-and-stick model of *trans*-decalin and convince himself that the molecule is rigid—the "flipping" process resorted to in cyclohexane is not possible here. The A form of menthol is disfavored by the large number of axial interactions. This is seen best in a scale model.

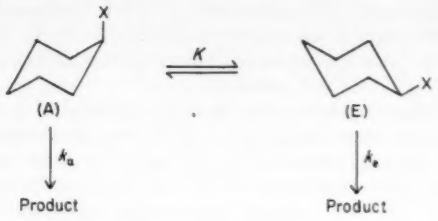


Figure 6. Reaction of mobile cyclohexane system.

If k_e is the specific rate of reaction of the equatorial isomer (E) and k_a the corresponding specific rate for the axial isomer (A), then the over-all rate of reaction will be

$$\text{Rate} = k_e\,[\text{E}]\,[\text{P}] + k_a\,[\text{A}]\,[\text{P}] \qquad \text{(i)}$$

where P is the product of all the concentrations, other than that of the cyclohexane substrate, which enter the kinetic equation. But empirically

$$\text{Rate} = k[\text{C}][\text{P}] \qquad \text{(ii)}$$

where k is the observed specific rate and [C] is the stoichiometric concentration of the cyclohexane substrate. Equating (i) and (ii) one obtains

$$k[\text{C}] = k_e[\text{E}] + k_a[\text{A}] \qquad \text{(iii)}$$

Dividing by [A] and putting [C] = [E] + [A], one gets

$$k([\text{E}] + [\text{A}])/[\text{A}] = k_e[\text{E}]/[\text{A}] + k_a \qquad \text{(iv)}$$

But [E]/[A] = K, the conformational equilibrium constant (Fig. 6). Inserting in (iv) one gets

$$k(K + 1) = k_eK + k_a \qquad \text{(v)}$$

or transposing,

$$k = (k_eK + k_a)/(K + 1) \qquad \text{(vi)}$$

Equation (vi) as written is mainly of heuristic interest in that it expresses the empirical rate constant k in terms of constants of more fundamental meaning, namely the rate constants k_e and k_a for the pure equatorial and axial isomers and the equilibrium constant K between these isomers. The equation may be readily tested for the extreme cases where the substrate is entirely in the equatorial form or entirely in the axial form. In the former case, $K = \infty$ and equation (vi) reduces to the form $k = k_e$[5] whereas in the latter case $K = 0$ and equation (vi) becomes $k = k_a$; in other words one obtains the required result that a purely equatorial isomer reacts at a specific rate k_e and a purely axial one at the specific rate k_a.

Winstein and Holness (*13*) use an alternative form of equation (vi) namely

$$k = N_ek_e + N_aK_a \qquad \text{(vii)}$$

where N_e is the mole fraction of cyclohexane molecules

[5] Dividing the numerator and denominator on the right-hand side of equation (vi) by K one obtains

$$k = \left(k_e + \frac{k_a}{K}\right)\Big/\left(1 - \frac{1}{K}\right)$$

whence

$$\lim_{K \to \infty} k = k_e.$$

in the equatorial conformation and N_a the mole fraction in the axial conformation. Since $N_e + N_a = 1$ and $N_e/N_a = K$, equation (vi) may be readily transformed into (vii) and vice versa.

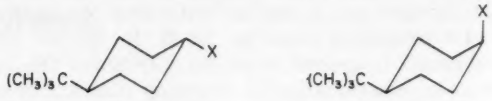
Either equation (vi) or (vii) is useful in estimating rate constants for systems which are not conformationally homogeneous. For example the question as to whether cyclohexyl tosylate (Fig. 3, X = p-$CH_3C_6H_4SO_2O$—) will undergo bimolecular elimination with base may be answered as follows: $k_e = 0$, since bimolecular ionic elimination requires the groups affected to be *anti*, i.e., axial. Therefore $k = N_a k_a$. N_a for tosylate is not known with certainty, but the estimates vary between 0.3 (*17*) and 0.1 (*13*). Thus the fact that the tosylate group is predominantly equatorial in cyclohexyl tosylate diminishes its rate of elimination with base by *at most* a factor of 10 as compared with the corresponding rate for a purely axial tosylate since, if Na = 0.1, $k = 0.1\ k_a$. In other words, despite its unfavorable conformation, cyclohexyl tosylate might be expected to undergo successful base-induced elimination, as indeed it does (*13*).

Equations vi, vii, and viii (below) may also be applied to equilibrium processes such as the dissociation of acids, in which case the rate constants k, k_e, and k_a are replaced by corresponding equilibrium constants (*15*).

Conformational Equilibria

Equation (vi) may be solved for K to give $K = (k_a - k)/(k - k_e)$ (viii). Equation (viii) may be used, at least in principle, to determine conformational equilibrium constants K (*cf.* Fig. 6) for a variety of groups. Such equilibrium constants are of interest from two points of view. One is that they give information on the size of groups, since the larger the group X, the greater would be expected to be its tendency to occupy the equatorial position and the larger should be K (see, however, below). The other reason for interest in the K-values is that one is often concerned, especially in the chemistry of natural products, with mobile cyclohexane systems having more than one substituent. Before one can decide on the reactivity of a given group in such a system, one must know whether the group is apt to be predominantly equatorial or predominantly axial and to what extent. (Once this information is known, reactivity can be calculated from equation (vi) or (vii).) To obtain this information one must know the K-values for all the pertinent substituents.

In order to evaluate K from equation (viii) it is necessary to know k_a and k_e as well as the empirical rate constant k for any given reaction in a cyclohexane system. Since in general the pure conformational isomers (A) and (E) (Fig. 6) are far too rapidly interconverted to be isolable, determination of k_a and k_e would seem to be a difficult task. A way out of the difficulty has been suggested by Winstein and Holness (*13*) who propose that k_e may be taken to be the rate constant for the reaction in question of a *trans*-4-*t*-butylcyclohexyl substituted compound and k_a the rate of a *cis*-4-*t*-butylcyclohexyl substituted compound (Fig. 7).[6] It is



trans-4-*t*-butyl substituted cyclohexyl compound (equatorial X)

cis-4-*t*-butyl substituted cyclohexyl compound (axial X)

Figure 7.

suggested (*13*) that the *t*-butyl group is so large that it will necessarily be in the equatorial position allowing the other substituent to occupy exclusively the equatorial position in the *trans* isomer and the axial position in the *cis*. (The difference between equatorial and axial *t*-butyl is estimated to be 5.6 kcal/mole (*13*).) Three additional assumptions are implied in this method of obtaining k_e and k_a: (1) The *t*-butyl group must not exert any polar influence at the reaction site, so that the rate constants obtained from the 4-*t*-butyl substituted cyclohexanes will be the same as those for the (unstable) equatorial and axial forms of cyclohexane itself. (2) By the same token, the *t*-butyl group must exert no direct steric influence on the reaction site. (3) The *t*-butyl group must not give rise to distortion of the ring, for if it does, the geometry, and therefore the specific reaction rates of the 4-*t*-butyl substituted compounds might be different from that of the pure forms of the unsubstituted cyclohexyl compound.

Evidence for the soundness of the first assumption comes from acidity measurements (*15*) of cyclohexanecarboxylic acid, pK = 7.82 in 66% dimethyl formamide, and *trans*-4-*t*-butylcyclohexanecarboxylic acid, pK = 7.79. If the *t*-butyl group exerted an appreciable polar effect, the two pK values would not be so similar. The second assumption (absence of direct steric effect) appears reasonable from molecular models. Both assumptions are also supported by the near identity of of rate of *cis*-3- and *trans*-4-*t*-butylcyclohexanol (both having equatorial OH) and *trans*-3- and *cis*-4-*t*-butylcyclohexanol (both having axial OH) in the acetolysis of their tosylates and the alkaline saponification of their acid phthalates (*13*). The third assumption—lack of deformation of the ring by the *t*-butyl substituent—is perhaps the weakest of the three. We shall discuss this assumption further below.

Using the method here outlined, several conformational equilibrium values have been determined by what we shall call the "kinetic method," i.e., application of equation (viii) determining k_e and k_a as indicated above. Free energy differences corresponding to the values so determined are included in Table 1. The value for the hydroxyl group has been determined using as probing reaction oxidation with chromic acid in 75% acetic acid (*13*) and acetylation with acetic anhydride in pyridine (*16*). The tosylate value comes from solvolysis rates (*13*) and from bimolecular displacement and elimination rates with thiophenolate (*17*); unfortunately the two values are not in good agreement. The p-nitrobenzoate value comes from saponification

[6] There are other possible ways of evaluating k_e and k_a. The *cis*- and *trans*-3-*t*-butylcyclohexyl substituted compounds have been used to obtain k_e and k_a, respectively (ref. (*13*)). The two *meso* forms of a 3,5-dimethylcyclohexyl substituted compound might also be used; in view of the great tendency of the methyl groups to avoid the diaxial conformation (in which there would be serious steric interaction between them), these groups would be equatorial and the remaining 1-substituent would be equatorial in one of the *meso* forms and axial in the other.

rates (*18*) and the bromide value from reaction rate with thiophenolate (*19*). The value for the carbethoxy group comes from saponification rates (*20*).

Several other methods have been used to obtain conformational equilibrium constants. A direct equilibration method is shown in Fig. 8. This method has been

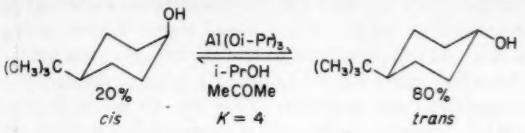


Figure 8. Direct equilibration.

applied (*21*) to hydroxyl (Meerwein-Ponndorf-Oppenauer type equilibration using aluminum isopropoxide-isopropyl alcohol-acetone) and to carbethoxy (*20*) using base-catalyzed epimerization;[7] the results are shown in Table 1. Unfortunately the method is of rather limited usefulness, since it cannot be applied to groups such as methyl which are not readily epimerized by chemical means. Fortunately, an "indirect equilibration method" has been discovered in the author's laboratory (*22*). This method is based on the observation that when *cis*- and *trans*-4-*t*-butylcyclohexanol are equilibrated by means of lithium aluminum hydride - aluminum chloride - 4-*t*-butyl-cyclohexanone, the equilibrium is displaced from the normal 20–80 position (Fig. 8) to one corresponding to over 99% of the *trans* isomer. Presumably the entity epimerized in this case is not the free alcohol, as in Fig. 8, but a solvated aluminum complex (Fig. 9). The position of

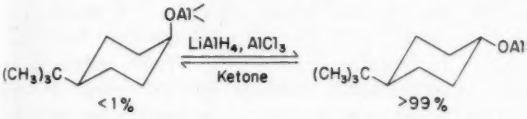


Figure 9. Equilibration of complex.

the equilibrium shown in Fig. 9 indicates that the free energy differences between the complexes is at least 3 kcal/mole. If another 4-substituted cyclohexanol is pimerized by the $LiAlH_4$-$AlCl_3$-ketone reagent, the situation depicted in Fig. 10 will obtain. Unless the

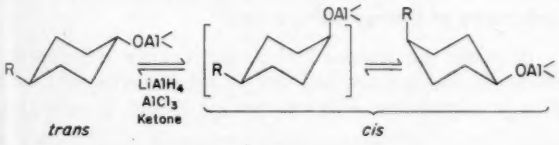


Figure 10. "Indirect equilibration."

substituent R is rather large, the conformation in brackets will make a negligible contribution and the ratio of *trans* to *cis* 4-substituted cyclohexanol found after hydrolysis of the complexes by the usual analytical methods (gas chromatography or infrared analysis) will give the conformational equilibrium constant directly. Using this method, the values for methyl and phenyl shown in Table 1 have been obtained by what may be called "indirect equilibration."

Two spectroscopic methods of getting at conformational equilibria may also be mentioned here. One (*23*) employs nuclear magnetic resonance spectroscopy. The NMR spectrum of a mobile molecule such as that depicted in Fig. 3 will usually not show lines due to the individual conformational isomers, since the velocity of interconversion of these isomers will be rapid[8] relative to the frequency difference to be expected between corresponding lines of the two isomers. Under these circumstances the Franck-Condon principle[9] does not hold, and the NMR spectrum will show lines due to average positions of pertinent atoms in the two conformations. This average position gives rise to a chemical shift which will be given by an equation analogous to (vii), namely $\delta = N_e\delta_e + N_a\delta_a$ (ix) where N_e and N_a have the same meaning as before and δ_e and δ_a are the chemical shifts for appropriate nuclei in the pure equatorial and pure axial conformations. This equation may be transformed into one analogous to (viii), namely $K = (\delta_a - \delta)/(\delta - \delta_e)$(x). The question as to how to evaluate δ_a and δ_e is solved exactly as in the kinetic method. An example is shown in Fig. 11.

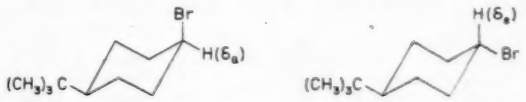


Figure 11. Chemical shifts.

Here δ_a is the chemical shift for the hydrogen near bromine in *cis*-4-*t*-butylcyclohexyl bromide, δ_e is the corresponding shift in the *trans* isomer, and δ is the observed shift in the mobile system cyclohexyl bromide (Fig. 3, X = Br). The success of the method depends on there being appreciable differences in chemical shift between equatorial and axial hydrogens (or other pertinent groups). In the case of the compounds shown in Fig. 11 this difference is about 40 cps (cycles /sec) at 60 mc (megacycles), and since chemical shifts may be measured accurately to about 1 cps, quite accurate equilibrium constants may be obtained by use of equation (x).

Infrared spectra have also been used to approach conformational problems (*6*). Here the Franck-Condon principle is obeyed and the equatorial and axial isomers give discrete spectra. By measuring the change of intensity of lines due to the two conformational isomers as a function of temperature, one may, by application of the van't Hoff equation, obtain the enthalpy (*not* free energy) difference between the two conformations. Infrared measurements have also been used (*25*) to measure conformational equilibrium con-

[7] The term "epimerization," though originally coined in sugar chemistry, is now used generally to denote change in configuration at one atom in a molecule with respect to another atom or other atoms. In the case shown in Fig. 8 the configuration (arrangement of the groups) about the carbinol carbon is changed, but the arrangement about the methane carbon (No. 4) remains the same. As a result, the relative configuration of the two carbon atoms is changed from *cis* to *trans*.

[8] NMR may actually be used to measure the height of the barrier to interconversion, *cf.* ref. (*24*).

[9] According to the Franck-Condon principle, the motion of the electrons from the ground state to the excited state in *electronic* spectra is so fast that the atoms do not have time to move during the transition; in other words the atomic arrangement in the excited state must be the same as in the ground state. In NMR spectra, however, the frequency of absorption is long compared to the time it takes for the E configuration (Fig. 3) to be transformed into an A conformation.

stants directly, making the assumption that the intrinsic intensity (the molar extinction coefficient) for a given band due to the equatorial isomer is the same in the *trans*-4-*t*-butyl substituted compound as in the unsubstituted cyclohexyl compound.

A number of conformational free energy differences between equatorial and axial groups obtained by these methods are summarized in Table 1. A few points

Table 1. Conformational Free Energy Differences Between Equatorial and Axial Substituents in Cyclohexane

Group	$-\Delta F$, (kcal./mole)	Temp. (°C)	Solvent	Method	Ref.
OH	0.8	40	75% AcOH	kinetic	(*13*)
OH	0.5	25	pyridine	kinetic	(*16*)
OH	0.9	25	water	[a]	(*35*)
OH	0 96	90	$CH_3CHOHCH_3$	equil.	(*21*)
OH	0.33[b]	25	water	calorim.	(*36*)
OH	0.4	20	CS_2	infrared	(*25*)
OAc	0.36	25	AcOH-Ac_2O	equil.	(*37*)
PNB[c]	0.9	25	80% Me_2CO	kinetic	(*18*)
OTs[d]	1.7	50	EtOH, AcOH, HCOOH	kinetic	(*13*)
OTs[d]	0.7	25	87% EtOH	kinetic	(*17*)
Br	0.7	..	none	[a]	(*38*)
Br	0.7	25	87% EtOH	kinetic	(*19*)
CH_3	1.6–1.8[b]	..	none	calorim.	(*29*, *30*)
CH_3	1.5–1.8	35	ether	equil.	(*22*)
C_6H_5	*ca.* 2.6	35	ether	equil.	(*22*)
COOEt	1.2–1.4[e]	25	70–100% EtOH	kinetic equil.	(*20*)
COOH	1.6-1.7		66% DMF[f]	[g]	(*15*)

[a] Indirect argument. [b] ΔH value. [c] *p*-Nitrobenzoate. [d] OTs (tosylate) is *p*-$CH_3C_6H_4SO_2O$—. [e] Tentative value. [f] DMF is dimethylformamide; data were also obtained in 80% methyl cellosolve. [g] Application of eqn. viii to acidity constants.

in this table are of special interest. For example, the considerable variation (by several hundred cal) of the value for hydroxyl (for which the largest number of different determinations happens to be available) might be a matter of some concern. It must be kept in mind, however, that the hydroxyl group is a group which may form hydrogen bonds either by donating or by accepting a hydrogen. If hydrogen bonds are formed with the solvent, this will give rise to stabilization of the system. Hydrogen bonds might be expected to be formed more readily when the hydroxyl group is equatorial, since it is then sterically more accessible. Therefore it is to be expected that hydrogen-bonding solvents might bias the conformational equilibrium of hydroxyl in favor of the equatorial form. This bias might be expected to be greater when the ring hydroxyl group is the hydrogen acceptor than when it is the donor, for steric hindrance to hydrogen bonding with axial hydroxyl would be expected to be stronger when the oxygen atom of the group is involved (since it is close to the ring) than when the hydrogen atom of the ring hydroxyl group is involved. The data in Table 1 would seem to bear this out, for one of the lowest ΔF values is obtained in a non-bonding solvent (carbon disulfide), an intermediate value is found in a hydrogen-acceptor solvent (pyridine) and the highest ΔF values are found in hydrogen-donor solvents (aqueous and alcoholic media). The same sort of situation pertains in the case of bromine which is more axial in pure cyclohexyl bromide than in aqueous ethanol. Infrared measurements of the relative areas of the bands due to equatorial and axial C-Br stretching (*23*) in various solvents do, in fact, suggest that solvents which are hydrogen-bond donors favor the equatorial conformation of bromine.

The fact that ΔF for bromine is much smaller than ΔF for methyl is also noteworthy. The van der Waals radius for methyl (2 Å) is almost the same as that for bromine (1.95 Å), and the two substituents are usually considered to be of almost equal size. Three factors are deemed to contribute to the apparently smaller size of bromine and its correspondingly greater tendency to occupy the axial position. One has to do with bond lengths: since the C-Br bond is considerably longer than C-C (1.95 Å versus 1.54 Å), the axial H-Br distance (2.67 Å) will be somewhat greater than the C-H distance (2.51 Å), as shown in Fig. 12. This means that despite

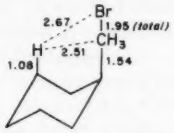


Figure 12. Interatomic distances in cyclohexyl bromide and methylcyclohexane (axial isomers).

the similarity in van der Waals radii of bromine and methyl, the interaction with the axial bromine will be somewhat less. A second point has to do with London forces.[10] Since bromine is so much more polarizable than carbon, there will be a London attractive energy between axial hydrogen and axial bromine much in excess of the corresponding energy between hydrogen and methyl. This London attraction will in part compensate for the van der Waals repulsion. A third argument has to do with the shape of the van der Waals radius. In bromine, the van der Waals radius is believed to be greater at the distance away from the bond than on the side near the bond. In methyl, on the other hand, the van der Waals interaction is about the same in all directions. Since for the diaxial interaction in cyclohexane because of the much greater distance of C—Br (1.95 Å) over C—H (1.08 Å) the interaction is largely on the "underside" of the bromine atom, the van der Waals radius will be shorter than usual. The same is not true for methyl.

Additivity of Energy Differences

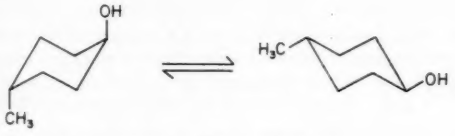
It might be assumed that the energy differences shown in Table 1 are additive, in other words that the energy required to shift two groups X and Y from the

[10] London forces are attractive forces of quantum mechanical origin between non-bonded atoms. They are responsible for the familar dip in the van der Waals potential curve, i.e., the fact that the potential energy of two non-bonded atoms is lower when they are at precisely the van der Waals distance from each other than when they are farther apart. The London forces are attractive; the energy varies as the inverse sixth power of the distance between the atoms concerned. In contrast, the more familiar van der Waals repulsive force leads to an energy term proportional to the inverse twelfth power of the interatomic distance. As a result, the repulsive van der Waals force is more important at very close range, but at a somewhat longer range (in the vicinity of the van der Waals radius) the attractive London force is more important. A classical picture of the London force may be obtained by imagining the electron clouds of two atoms polarizing each other so that they, together with the positively charged nuclei, form two dipoles oriented antiparallel. Such dipoles will, of course, attract each other.

equatorial into the axial position would be the sum of shifting X and Y individually into axial positions (assuming no interaction between X and Y in either of the conformations of the molecule containing both groups). This assumption has been tested with somewhat equivocal results. Two examples are shown in Figs. 13 and 14. The experimental ΔF values were obtained by ap-

ΔF calc'd $= \Delta F_{OH} - \Delta F_{CH_3}$
$= -0.5-(-1.5)$
$= 1.0$ kcal/mole
ΔF found $= 1.2$ kcal/mole

Figure 13. Calculated free energy difference for *cis*-4-methylcyclohexanol.



ΔF calc'd $= \Delta F_{OH} + \Delta F_{CH_3}$
$= -0.5-1.5$
$= -2.0$ kcal/mole
ΔF found $= -1.1$ kcal/mole

Figure 14. Calculated free energy difference for *trans*-4-methylcyclohexanol.

plication of equation (viii) using for k the experimental rate constant for the appropriate reaction (in this case acetylation) of the methylcyclohexanol in question. Experimental and calculated ΔF values for several compounds are further compared in Table 2. It may be seen that the agreement is by no means uniformly satisfactory.

Table 2. Conformational Energy Differences for Disubstituted Compounds—Comparison of Calculated and Experimental Values

Compound	Reaction	ΔF calc'd. (kcal/mole)	ΔF found (kcal/mole)
cis-4-methylcyclohexanol	acetylation	1.0	1.2
trans-4-methylcyclohexanol	acetylation	−2.0	−1.1
cis-3-methylcyclohexanol	acetylation	$-\delta$, (large)	$-\delta$, (large)
trans-3-methylcyclohexanol	acetylation	1.0	1.1
cis-4-methylcyclohexyl tosylate	thiophenolate substitution	0.8	−0.1
cis-4-methylcyclohexyl tosylate	thiophenolate elimination	0.8	0.9
trans-4-methylcyclohexyl tosylate	thiophenolate (total rate)	−2.2	−2.8
cis-3-methylcyclohexyl tosylate	thiophenolate (total rate)	$-\delta$, (large)	−3.0
trans-3-methylcyclohexyl tosylate	thiophenolate substitution	0.8	1.2
trans-3-methylcyclohexyl tosylate	thiophenolate elimination	0.8	0.7
cis-4-methylcyclohexyl bromide	thiophenolate substitution	0.8	0.4
cis-4-methylcyclohexyl bromide	thiophenolate elimination	0.8	0.5

[11] This subject has also been recently discussed by HÜCKEL W., ET AL. *Ann.*, **634**, 142 (1959). See also SANDRIS, C., AND OURISSON, G., *Bull. Soc. Chim. France*, **1958**, 1524.

Deformation of Ideal Chair Form[11]

A likely weakness of our treatment of mobile systems is assumption (3) above which amounts to saying that substituted cyclohexanes are all perfect chairs. However, it is well known form Westheimer's pioneering calculation of barriers to biphenyl racemization (*26*) that any sort of steric interaction in a molecule will tend to be minimized by distortion of the normal bond angles. This is because the energy needed to bring about small angular deformations is small compared to the energy needed to bring groups into proximity much closer than the sum of their van der Waals radii. Thus any interaction between groups in a substituted cyclohexane—such as the interaction of an axial group with axial hydrogens—will give rise to a deformation of the chair, and the degree of deformation will increase with the severity of the interaction which causes it. Thus 1,1,3,3-tetramethylcyclohexane (1-3 diaxial methyl interaction) or *cis*-1,4-di-*t*-butylcyclohexane (axial *t*-butyl interaction) might be expected to be deformed quite severely. As a result of such deformation, group interactions of the kind shown in Fig. 14 may be far from additive. Putting the methyl group in an axial position may deform the chair in such a way as to make it either easier or more difficult for the hydroxyl to occupy the axial position than it is in cyclohexanol itself.

Some concrete evidence for the presence or absence of such deformation may now be examined. The rate of acetylation of 4,4-dimethylcyclohexanol (Fig. 15,

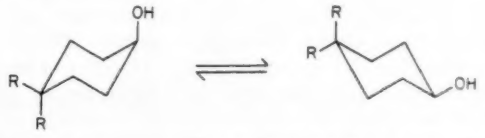


Figure 15. Cyclohexanol and 4,4-dimethylcyclohexanol. R = CH_3, k = 8.43×10^{-5} l/mole/sec. R = H, k = 8.37×10^{-5} l/mole/sec.

R = CH_3) has been measured (*16*) and found to be identical, within the limits of experimental error, with the corresponding rate for cyclohexanol (Fig. 15, R = 4). Since both forms in 4,4-dimethylcyclohexanol contain an axial methyl group, this finding suggests that this group does not deform these forms appreciably in comparison to the corresponding forms of cyclohexanol itself. A different conclusion is suggested, however, by the finding (*27*) that the equilibrium constants for the dissociation of cyclohexanone cyanohydrin, 4-methylcyclohexanone cyanohydrin and 4,4-dimethylcyclohexanone cyanohydrin differ appreciably (Table 3). The possible cause for this contrast lies in the fact

Table 3. Relative Dissociation Constants of Cyclohexanone Cyanohydrins (*27*)

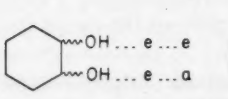
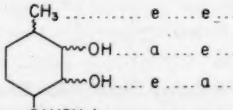
Cyclohexanone	Dissociation constant
unsubstituted	1.0
4-methyl	0.6
4,4-dimethyl	2.5

that the deformation produced by an axial 4-methyl group (total interaction 1.5 kcal/mole., *cf.* Table 1 is likely to be small. In a reaction such as acetylation

where the ground state and transition state differ only at the acetyl function which is remote from the ring, the effect of such a deformation will be negligible. But in the cyanohydrin reaction where the geometry of the ketone (sp^2) and cyanohydrin (sp^3) differ greatly at one of the ring atoms, even a small deformation of the ring may produce an appreciable change in the equilibrium.

Deformations of the chair form might be expected in 1,2-disubstituted cyclohexanes where there is a skew interaction of the substituents in the e,a-*cis* and e,e-*trans* positions. In an undeformed chair the distance between e,a-*cis* and e,e-*trans* substituents is exactly the same. It has already been pointed out, however (*28*), that the chair may be readily deformed so as to make the *cis*-bonds approach each other, this being the reason why a five-membered ring (nearly planar) can be fused *cis* to a six-membered ring more readily than *trans* in most cases. By the same token, the chair may be readily deformed so as to bend *trans*-e,e groups (but not *cis*-e,a groups) away from each other, relieving their steric compression. There are some data in the literature to suggest that such "bending away" does indeed occur. Thus Beckett, Pitzer, and Spitzer (*29*) were able to calculate the relative entropies of *trans*-1,2-, *cis*- and *trans*-1,3-, and *cis*-, and *trans*-1,4-dimethylcyclohexane considering only entropies of mixing (of non-identical conformational isomers and *dl*-forms) and symmetry numbers. However, in the case of the *cis*-1,2-dimethylcyclohexane, the calculated relative entropy was too high, unless allowance was made for a decrease in rotational entropy due to interference of the adjacent methyl groups. No such decrease was observed in the *trans*-1,2-dimethyl isomer. This is unreasonable on the basis of a perfect chair in which e,e- and e,a-methyl groups are equidistant, but it is explainable in terms of a deformed chair in which the e,e-groups are bent away from each other far enough to avoid mutual interference but the e,a-groups are in their normal, crowded positions. The fact (*30*) that *cis*-1,2-dimethylcyclohexane differs in heat of combustion from the *trans*-epimer by a somewhat greater amount than do the epimeric 1,3- and 1,4-dimethylcyclohexanes from each other is consistent with the idea of a deformation in the *trans* isomer which reduces the interference energy.

Table 4. Frequency Difference Between Bonded and Unbonded Hydroxyl Groups in 1,2-Cyclohexanediols

	I	II	III	IV	V	VI
	OH	e	e			
	OH	e	a			
	CH_3		e	e	a	a
	OH		a	e	a	e
	OH		e	a	e	a
	$CH(CH_3)_2$		e	e	e	e
$\Delta\tilde{\nu}$, cm^{-1}			32	38	56	50	54	36

Another example of what may be a deformation of the chair is found in the infrared spectra of the four epimeric *cis*-2-hydroxymenthols (*31*), although the evidence was interpreted differently by the original authors (*31*). The pertinent data are shown in Table 4. The spectra of the 2-hydroxycyclohexanols (1,2-cyclohexanediols) show a band due to intramolecularly bonded OH as well as a free hydroxyl stretching band. The separation between the two bands, listed in Table 4, is a measure of the strength of the intramolecular hydrogen bond: the stronger the bond, the bigger the separation (*32*, *33*). *cis*- (II) and *trans*-2-hydroxycyclohexanol (I) differ only slightly in this separation (*32*). If both were perfect chairs, the separation would be the same. The slight difference suggests that the hydroxyl groups in the *cis*-isomer (II) are closer together than in the *trans* (I)—either because the *cis*-hydroxyl groups bend toward each other or because the *trans*-hydroxyl groups bend away from each other. In three of the four *cis*-2-hydroxymenthols (hydroxyl groups *cis* to each other), the hydrogen bond is substantially stronger (evidenced by larger $\Delta\tilde{\nu}$) than in *cis*-2-hydroxycyclohexanol. This may be taken to mean that the equatorial alkyl group adjacent to the equatorial hydroxyl in *cis*-2-hydroxymenthol (III), *cis*-2-hydroxyneomenthol (IV) and *cis*-2-hydroxyisomenthol (V) causes the equatorial hydroxyl group to bend away from the alkyl group and toward the other hydroxyl group, thus strengthening the hydrogen bond. Only in *cis*-2-hydroxyneoisomenthol (VI) where there is no equatorial alkyl adjacent to the equatorial hydroxyl group is the hydrogen bond of approximately the same strength as in *cis*-2-hydroxycyclohexanol itself, suggesting that both these molecules are nearly perfect chairs.

Experiments designed to demonstrate possible deformation of the chair form of substituted cyclohexanes are presently under way in the author's laboratory. If such deformations turn out to be general, they will be important in such calculations as that of the conformational equilibrium of *trans*-1,2-dibromocyclohexane (e,e $\rightleftharpoons$ a,a) from dipole moments (*34*). This calculation involves the assumption that the dipole moment of the e,e-form is identical with the observed moment of *cis*-1,2-dibromocyclohexane (e,a)—an assumption which is valid only if the e,e-groups are not bent away from each other more than the e,a-groups.

Acknowledgment

The author's research in the area of conformational analysis is supported in part by the Office of Ordnance Research, U. S. Army (Contract DA-11-022-ORD-2279), in part by the National Science Foundation (Grant NSF G-7371), and in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said funds.

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A Separation and Identification Experiment for Elementary Organic Chemistry Laboratory

Although a separation problem is a desirable means of drawing together many of the techniques learned in the first organic course, a full-scale separation and identification is too time-consuming and precarious, while a simple separation is not enough of a challenge. For two years we have tried a formalized and limited separation and identification experiment as a year-end project and can now recommend such an approach to others facing the same dilemma.

The student chooses a test tube containing roughly 10 g each of two unknowns, which may or may not form a single phase. He is told that the two are selected from *two* of three groups: 1 (*a*) a primary amine or (*b*) a tertiary amine; 2 (*a*) an aldehyde or (*b*) a ketone; and 3 (*a*) an acid or (*b*) a phenol. The components are to be separated, their physical properties determined, their categories assigned, and one specified derivative prepared for each. The routine laboratory work has included most of the characterization tests, but otherwise the students are left on their own with the collection of texts and references used by the organic qualitative analysis course.

The derivatives specified are: 1 (*a*) benzenesulfonamide, (*b*) methiodide; 2 (*a*) and (*b*) 2,4-dinitrophenylhydrazone; 3 (*a*) anilide, (*b*) aryloxyacetic acid. The table gives a list of pairs of unknowns not found to be too difficult. The requirement is not that the unknowns necessarily be identified, but that the remaining possibilities be evaluated. Students are told that the unknowns are all to be found in the tables in at least one of the standard texts. They may ask for any reagents they wish, but knowns for the tests are supplied at the choice of the instructor.

Examples of Possible Combinations of Unknowns

Benzaldehyde and benzoic acid
Quinoline and furfural
Acetophenone and β-naphthol
Aniline and *p*-nitrobenzoic acid
N,N-dimethylaniline and crotonaldehyde
N,N-diethylaniline and acetophenone
α-Naphthylamine and *p*-anisic acid
Aniline and cinnamic acid
o-Toluidine and phenol
Tri-*n*-butylamine and isobutyraldehyde
Isoquinoline and 2-pentanone
α-Picoline and *o*-cresol
Butyraldehyde and butyric acid
3-Pentanone and benzoic acid
Cyclohexanone and *p*-cresol
o-Toluidine and *o*-cresol

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Inorganic Polymerization Reactions

III. Coordination polymerization

In the first and second articles in this series, two general methods for preparing inorganic polymeric compounds were discussed; these processes are, in essence, analogous to the better known reactions leading to organic polymers. Inorganic polymers can be formed (*a*) by condensation reactions, involving elimination of simple molecules to yield higher molecular weight aggregates, and (*b*) by addition polymerization, in which the repeating units are identical with the monomers from which the polymers are derived. The processes leading to the formation of polymeric materials containing coordinated metal ions are not readily classified in either of the above categories, and it seems justifiable to consider this aspect of the subject in a separate section.

Polymers containing coordinated metal ions can be divided into three general categories:

(1) Some result when metal ions and ligands combine. The possibility of using reactions of this type depends primarily on the fact that transition metal ions are polyfunctional in character. Such ions are capable of accepting more than one pair of electrons and consequently in many cases, reaction with polyfunctional donor molecules will result in chain or cross-linked polymeric structures.

(2) Some are obtained from metal ions and preformed polymeric ligands having coordination sites.

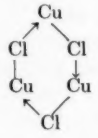
(3) Some are obtained when monomers containing coordinated metal ions are polymerized through functional groups.

Metal Ions and Suitable Multidentate Ligands

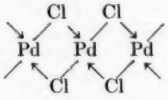
In theory, any donor group which contains two pairs of unshared electrons can be used to link metal ions. Under certain circumstances, when the stereochemistry of the donor group and the metal ion are favorable, chelate ring formation occurs. Polymeric compounds are formed when both pairs of electrons are on the same atom in the coordinating group (e.g., Cl, OH), when the electron pairs are on atoms linked directly to each other (e.g., CN), or when the donor atoms are widely separated in the ligand molecule.

Simplest examples of polymeric materials resulting from coordination are the dimers of aluminum and ferric chlorides, found in the vapor state. Each metal atom is surrounded tetrahedrally by four chlorine atoms (*108*), i.e.,

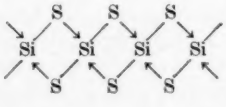
Similarly, recent infra-red (*109*) and electron diffraction (*110*) studies point to the presence of trimers in the vapor of cuprous chloride.



Discrete molecules of palladium(II) chloride do not exist in the solid state, but infinite chains of planar $PdCl_4$ groups sharing opposite edges make up the structure (*111*).



The structure of silicon sulfide is somewhat analogous, consisting of infinite chains of SiS_4 tetrahedra sharing opposite edges.



Similarly, cyanide groups can act as bridges between metal atoms giving polymers of varying complexity depending on the relative numbers of metal atoms and cyanide groups and on the stereochemistry of the metal involved. For instance, in silver and gold cyanides, the metals have only two coordination positions at 180° from each other and linear polymers consisting of alternate metal atoms and cyanide groups result.

$$\rightarrow M{-}C{\equiv}N \rightarrow M{-}C{\equiv}N \rightarrow M{-}C{\equiv}N \rightarrow$$
(M is Ag, Au)

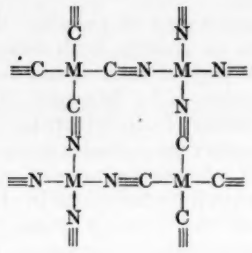
The cyanides of metals capable of forming four coplanar bonds, e.g., divalent Pd, Pt, Ni, and Cu, consist of infinite layer lattices in which alternate metal atoms are coordinated to four nitrogen atoms and four carbon atoms.

Based upon a paper presented before the Division of Polymer Chemistry at the 134th Meeting of the American Chemical Society, Chicago, Ill., September, 1958.

This is the third in a series of three papers on this topic to be published in THIS JOURNAL. For the first and second papers, see J. CHEM. EDUC., **37**, 2, 86 (1960).

Literature citations and tables in this paper are numbered consecutively with those in the earlier papers.

[1] At present, serving as Scientific Attaché at the American Embassy, Bonn, Germany.

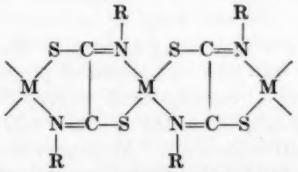


When the metal ion can adopt octahedral configuration, three dimensional arrays are possible. Although solutions of the alkali and alkaline earth ferrocyanides contain discrete $Fe(CN)_6^{4-}$ ions, addition of transition metal salts often leads to the formation of highly colored insoluble precipitates, e.g., Prussian Blue, Turnbull's Blue, and the like. X-ray studies on these compounds are in agreement with highly polymeric three dimensional structures in which coordination by both the carbon and nitrogen atoms of the cyanide group is important (*112*).

It is well known that many other simple groups, e.g., NH_2, NH, NO_2, etc., are capable of acting in a similar manner.

In many cases it has been observed empirically that chelation with metal ions greatly enhances the thermal stability of organic ligands.[2] Monomeric chelate compounds are obtained with coordinating compounds such as ethylene diamine but polydentate agents can give rise to polymeric compounds. The degree of cross-linking in any polymer of this type is governed by the coordination number of the metal and the number of coordinating centers of the ligand. Combination between a bis-(bidentate) ligand and a tetra-coordinate metal ion, or between a bis-(tridentate) ligand and a hexacoordinate metal ion will lead to linear polymers, if the two bidentate functions are unable to coordinate to the same metal ion. A bis-(bidentate) ligand and a hexacoordinate ion or a polyfunctional ligand with a tetracoordinate metal, on the other hand, could give highly cross-linked polymeric products. A hexacoordinate metal could be used with bidentate ligands to prepare linear polymers if two of the coordination positions could be blocked with unreactive groups.

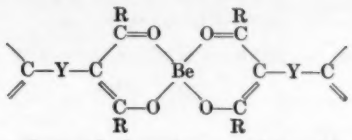
Tetracoordinate metal ions such as Cu(II) and Ni (II) react with dithio-oxamide and substituted dithio-oxamides (*113*, *114*) giving insoluble compounds of unknown molecular weight which undoubtedly contain long chain molecules of the type



(where R is H, CH_3, $C_6H_5CH_2$, $HOCH_2CH_2$, etc.)

[2] W. C. Fernelius and B. E. Bryant (*Inorganic Syntheses*, **5**, 105 (1957)) have shown that many metal acetylacetonates can be distilled without decomposition. The boiling point of acetylacetone is 139°C, whereas the Th(IV) derivative distils at 260–270°C (10 mm) and the Ni(II) complex at 220–235°C (11 mm).

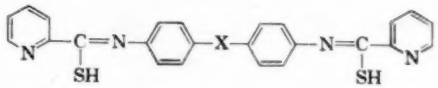
The preparation of linear polymers from beryllium ions and bis-(β-diketones) is described in a patent (*115*).



(where Y is a divalent hydrocarbon containing at least 4 carbon atoms)

Fernelius and co-workers (*116*) have studied extensively the coordination chemistry of bis-(β-diketones), especially the effect of substituents in the ligand and nature of the metal ion on the thermal stabilities and molecular weights of the resulting polymers.

A degree of polymerization of the order of fifteen has been observed when bis-(α-thiopicolinamides) based on



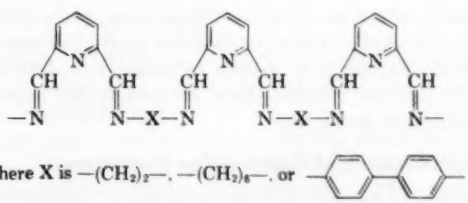
are treated with the acetylacetonates of copper, nickel, and zinc (*117*). The copper phthalocyanine preparation has been modified to give linear polymers by replacing either all or part of the phthalic anhydride used in the conventional synthesis by tetrafunctional pyromellitic dianhydride or 3,3′,4,4′-tetracyanodiphenyl ether (*118*, *119*).

Many of the products that have been obtained at the present time from processes described above have desirable thermal characteristics but are very brittle. To some extent, this can be traced to the highly directional nature of the bonding between the ligand and the metal ions. Some progress has been made toward producing more plastic materials by introducing elastic groups, such as carbon chains, into the ligand.

Some of the ligands that have been proposed as bases for the production of coordination polymers are listed in Table 3.

Metal Ions and Polymeric Ligands

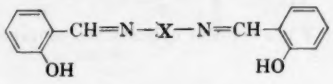
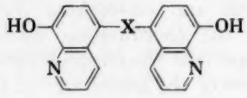
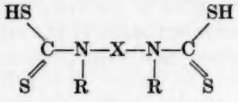
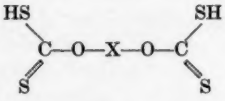
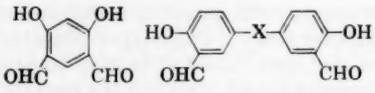
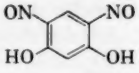
Production of polymers using preformed polymeric ligands has not yet been studied to any great extent. The literature, however, contains some interesting applications of this second general method. Lions and Martin (*120*) have prepared polyterdentate ligands by the reaction of pyridine-2,6-dialdehyde and diamines such as ethylenediamine hexamethylenediamine, and benzidine. The ligands, considered to have the structure



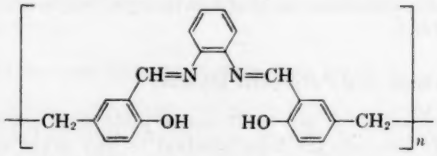
where X is $-(CH_2)_2-$, $-(CH_2)_6-$, or

give polymers of unknown molecular weights when treated with divalent copper or iron salts. Similarly Marvel and Tarköy (*121*) have prepared polymeric

Table 3. Polyfunctional Ligands (Polydentate Coordinating Agents)

bis-(β-diketones)	$RCOCH_2CO—X—COCH_2COR$ $(RCO)_2CH—X—CH(COR)_2$
bis-(α-amino acids)	$HOOC—\underset{NH_2}{CH}—X—\underset{NH_2}{CH}—COOH$
bis-(salicylaldehyde)-diimines	
bis-(8-hydroxyquinolines)	
bis-(dithiocarbamates)	
bis-(xanthates)	
bis-(o-hydroxyaldehydes	
bis-(nitroso phenols)	
bis-(glyoximes)	$RC(:NOH)C(:NOH)—X—C(:NOH)C(:NOH)R$

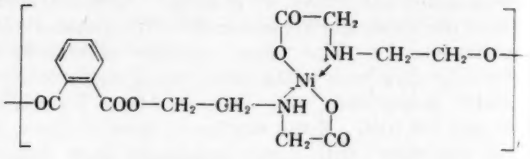
Schiff bases with molecular weights in the region of 10,000. For example, treatment of 5,5′-methylene-bis-(salicylaldehyde) with *o*-phenylenediamine gave the polytetradentate ligand



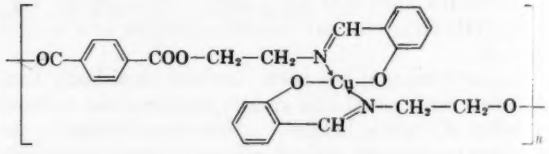
which gave polymetallic chelates with Cu(II), Zn(II), etc. Analogous reactions have been carried out by Bayer (*122*) using polymeric Schiff bases obtained from glyoxal and either 2,6-diamino-*p*-cresol or 2,4,6-triamino-phenol. It is also possible that some of the naturally occurring polymers, i.e., certain proteins and the like, could function similarly, but interaction with metal ions has not been examined extensively from this point of view. However, Mester (*123*) has converted polysaccharides, e.g., starch, cellulose, etc., into formazanes and shown that these substances are capable of complexing metal ions.

Polymerization of Coordination Monomers

High molecular weight compounds containing coordinated metal ions can be prepared when the ligand contains functional groups capable of undergoing conventional addition or condensation reactions. If the ligand contains an ethylenic side-chain, the usual addition polymerization may be possible. Vinyl ferrocene has been shown to undergo both homo- and co-polymerization with vinyl monomers and dienes (*124*), and although *trans*-cinnamoyl ferrocene does not homopolymerize, a variety of copolymers have been obtained (*125*). On the other hand, Bailar and co-workers (*126*) have carried out polyesterifications of coordination compounds having alcoholic functions in the ligand. The reaction between nickel bis-(*p*-hydroxy ethyl glycine) and phthalic anhydride in vacuum at 170° gave a low molecular weight polymer of the type:



while dimethylterephthalate and copper bis-(salicylidene ethanolamine) gave a product with the structure:



The possibilities for wide variation in both ligand and metal atom makes the field of coordination compounds particularly attractive for the preparation of polymeric materials.

Conclusion

Numerous methods are available for the preparation of purely inorganic polymers, but these compounds are usually highly cross-linked and involve strongly directional bonds. In this form, they offer little hope for application as useful high temperature stable fluids and the like. On the other hand, with the increasing emphasis on high temperature stability, it is apparent that purely organic polymers cannot meet the required specifications. It seems likely that progress will be made in the field of mixed inorganic-organic polymers, where incorporation of inorganic substances may enhance thermal stability but flexibility will be given by organic groups. The silicone polymers are outstanding examples of products of this type.

In the polymer field, inorganic chemists at the present time find themselves in essentially the same position occupied by the organic chemist some twenty years ago. The increasing interest in this subject will undoubtedly lead to a refinement of preparative methods. Probably, conventional polymerization techniques can be adapted to the special conditions of mixed inorganic-organic systems. More precise methods will also be necessary for the evaluation of the physical characteristics of the resulting products.

Acknowledgment

The authors wish to acknowledge help received during the preparation of this article from Dr. J. C. Bailar, Jr., and Dr. D. F. Martin, both of the University of Illinois.

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Grand Rapids, Michigan

Determination of Solubility

A laboratory experiment

During the past several years we have conducted a research program on the freshman level designed to improve instruction in general chemistry. Specifically, it has been our intention to develop a series of quantitative and/or unknown-type experiments. Such experiments emphasize the quantitative aspects of chemistry and put a premium on good laboratory technique. They interest even the apparently disinterested student and at the same time challenge the best of them.

Our procedure has been to examine critically all published experiments and other literature on a subject, and then, if possible, to improve upon the best available experiment or devise a new one to accomplish a similar purpose. Whenever possible, it has been our objective to develop a laboratory exercise which is adaptable to an unknown substance, and to challenge the student to identify it through his work in the laboratory. Two such experiments, the products of our freshman research program, have been described.[2,3]

There is a scarcity of good, elementary experiments on the properties of liquids and solutions. One found in a few laboratory manuals deals with the determination of the solubility curve of a salt whose identity is known to the student. It was our opinion that such an experiment has merit because it effectively teaches the meaning of a saturated solution and it affords the student an opportunity to learn the value of a graphical presentation of laboratory data. Eddy has recently described such an experiment on the determination of the solubility curve for borax by titration.[4] We proposed to study the methods for determining the solubility curve of a solute, particularly with a view to finding a procedure which could be used by the student on an unknown solute.

For the purpose of this study only water was considered for the solvent and the common salts as solutes. Preliminary investigations in the laboratory showed that, if fairly accurate results are to be expected in the usual 2–3 hour laboratory period, the preferred method for determining the solubility of a solute at various temperatures is to find the temperature at which a solution of known composition is saturated, that is, at which the solute begins to crystallize out of solution.

In the time available for this work seven salts were tried. The solubility curves of these were determined in triplicate. Four of these salts (KBr, $KClO_3$, KNO_3, and $K_2Cr_2O_7$) were found to give results very close to the values listed in the ninth edition of Lange's "Handbook of Chemistry." The three other salts which were tried (K_2SO_4, NH_4Cl, and $AlPO_4$) gave erratic results, probably because of hydrate formation or supersaturation of their solutions.

It was our objective to work out the details of procedure so that reliable results could be obtained by the average student with an unknown salt. This was especially important because of the wide variation in solubilities of these salts. The procedure given below

[1] This paper reports the work done by Pruiksma and Heerema as part of their freshman year's work at Calvin College.

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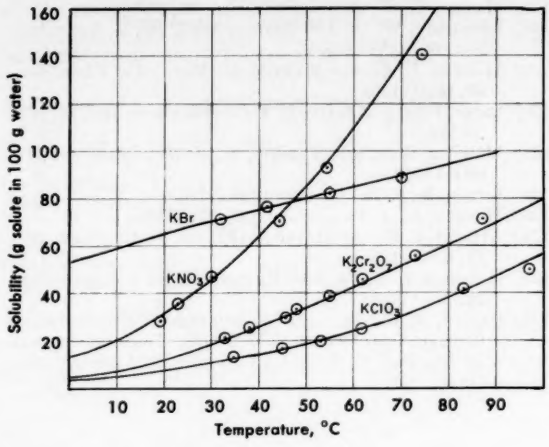

Solubility curves.

has been tested in several classes during the past two years with satisfactory results.

The Experiment

Fit an 8-in. test tube with a two-hole stopper holding a 110°C thermometer extending to within 1/4 in. of the bottom of the tube. A glass stirring rod with a loop at its lower end extends out of the test tube through the second hole in the stopper, and should be of such diameter as to slide easily through the stopper. Fill a 400-ml beaker 3/4 full of water, set it on a tripod or iron ring with an asbestos screen, and start heating it to boiling. Meanwhile weigh the test tube, without stopper, on the analytical balance to the nearest centigram. (This is most conveniently done by hanging the tube with a loop of copper wire from the balance pan support.) Obtain from your instructor a small envelope containing about 5 g of an unknown salt, empty it into the weighed test tube, and weigh it again.

Add to the tube exactly 3 ml distilled water, measured with a buret or graduated pipet. Attach the stopper with thermometer and stirrer, and clamp it in such a way that the level of solution in the tube is the same as the level of water in the beaker. While stirring well, warm the solution until all the solid is dissolved. If it has not dissolved when the water in the bath is boiling, add exactly 1 ml more distilled water, or as much more as is necessary to dissolve the salt. Be careful not to add more water than is absolutely necessary, and keep a record of the amount of water added. Also, do not keep the solution hot any longer than is necessary in order to prevent excessive evaporation of the water. After the salt has dissolved, raise the tube out of the water bath and allow it to cool, stirring the solution continuously. Record the temperature at which the first crystals appear in the solution. Repeat the warming and cooling to obtain a check result.

Now add 1 ml more distilled water, again heat as before to dissolve all solid, allow to cool, and again determine the saturation temperature. Further additions of water, 1 ml at a time, should be made, and saturation temperatures determined down to 30°C or less. If it is found that the saturation temperature drops rapidly after the first addition of 1 ml water, it is advisable to add only 0.5 ml in order to get as many points as possible for the solubility curve. On the other hand, if it appears that the saturation temperature drops very slowly with additions of 1 ml water, you may increase the water additions to 2 or 3 ml.

When all the readings have been made, record them on the report sheet, noting carefully the total amount of water as solvent for each temperature recorded. Calculate the concentration of each solution in terms of grams of salt per 100 g water, and record these values also. Then plot on a sheet of graphing paper, properly labeled, the concentration as ordinate against the temperature as abscissa.

Typical Student Results

A typical set of student data for the solubility of the four salts is found in the table. This tabular form for reporting experimental data and the calculated solubilities is required of each student, as well as a plot of the results.

Data Sheet and Typical Results

	Solute (g)	Water (g)	Solution concentration (g solute per 100 g water)	Saturation temp. (°C)
KBr	5.33	6	88.8	70
		6.5	82.0	55
		7	76.2	41.5
		7.5	71.0	32
$KClO_3$	4.94	10	49.4	97
		12	41.2	83
		20	24.7	61.5
		25	19.7	53
		30	16.5	45
		40	12.3	34.7
KNO_3	5.60	4	140	74
		6	93.2	54
		8	70	44
		12	46.7	30
		16	35	23
		20	28	19
$K_2Cr_2O_7$	5.01	7	71.6	87
		9	55.7	73
		11	45.6	62
		13	38.5	55
		15	33.4	48
		17	29.5	46
		20	25.1	38
		24	20.9	33

The figure shows how the determined values (circled) compare with the data in the literature, represented by the curves.

Ingenious theoretical superstructures live in constant dread of factual termites that continually gnaw at their foundations. They topple at the first inconsistency with observation. Concepts glory only in a relatively short term of office. We have witnessed the kaleidoscopic changes from Genesis to Darwin, from Ptolemy to Copernicus, from Boyle to van der Waals, from Newton to Einstein. This does not necessarily mean that no statements can be made about reality. It just means that science herself deals in temporary hypotheses of perfection at any given moment.

—R. G. H. Siu *in "The Tao of Science"*

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Samuel B. Knight,
and **Charles N. Reilley**
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Chapel Hill

Simultaneous Spectrophotometric Determination of Cobalt and Chromium

A student experiment

Many undergraduate courses in quantitative analysis now include an experiment to present spectrophotometric analysis for one component. An extension of such experiments to two-component analyses introduces the student to the problems encountered in the general case of multi-component analyses, and serves as an illustration of the ideas of linear dependence of several variables applied to the description of a physical system, a concept in quantitative analysis often encountered only in textbook problems.

This paper presents a summary of the theory and procedure applicable to two-component spectrophotometric analysis and describes a system which has been found very convenient for student instruction in this laboratory. The necessary stock solutions are easy to prepare (no buffers are required) and are quite stable for long periods of time. The unknowns as issued are ready for direct absorbance measurements and, though this is somewhat artificial from an analytical point of view, the experiment serves to present the essential spectrophotometric features of the problem as distinct from the preparation of the sample as such. Other systems have been described, such as the analysis of steel for Cr and Mn (*1*), which differ in these respects. A student experiment using the two-component method for the determination of the dissociation constant of methyl red and a two-component analysis in the ultraviolet region have previously been described in THIS JOURNAL (*2*, *3*).

The student should be familiar with the general procedures of one-component spectrophotometric analysis based on the Boguer-Beer equation $A = abc$, where A is the absorbancy, a is the absorbancy index, b is the length of the light path through the cell, and c is the concentration of the absorbing substance. Since for most applications the value of b is held constant throughout an experiment, we shall define and use the quantity $k = ab$ throughout this paper.

Now in the subsequent discussion we shall consider only systems for which the total absorbancy of a mixture for a given wave length is the sum of the absorbancies which would be measured for each of the components separately at the same concentrations present in the mixture. That is, for a mixture of n components the absorbancy at the ith wavelength is

$$A_i = \sum_{j=1} k_{ij}c_j \qquad (1)$$

where the i's refer to wavelengths and the j's to components. This linear relationship must be checked experimentally, and when it is found to exist for a two-component system the unknowns c_1 and c_2 are completely defined by the two equations

$$\begin{aligned} A_1 &= k_{11}c_1 + k_{12}c_2 \\ A_2 &= k_{21}c_1 + k_{22}c_2 \end{aligned} \qquad (2)$$

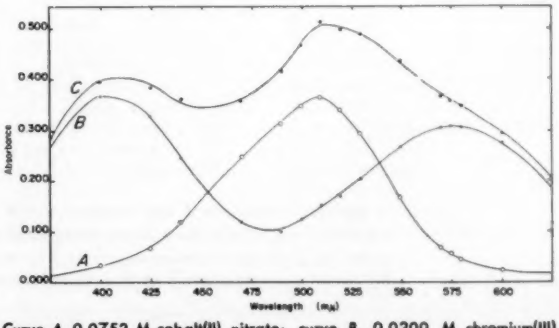
The experimental task then is to check for linearity, make an appropriate choice of wavelengths at which to measure A_1 and A_2, and to evaluate the k_{ij}'s.

The Experiment

Solutions. Stock solutions of cobalt (II) nitrate, 0.188 M, and chromium(III) nitrate, 0.0500 M, are provided in the laboratory. By reason of the method of preparing unknowns, it is not necessary for the solutions to be standardized, but they should be as close to the stated molarity as they can be prepared with graduated cylinder and laboratory trip scales.

From the stock solutions the following are prepared by appropriate dilutions: 0.0376 M, 0.0752 M, 0.1504 M, cobalt; 0.0100 M, 0.0200 M, 0.0400 M chromium; and one mixture that is 0.0752 M in cobalt and 0.0200 M in chromium.

Absorption Spectra. The absorption spectra of the 0.0752 M cobalt solution, of the 0.0200 M chromium solution, and of the mixture prepared above are taken. Adequate spectra can be obtained by making measurements at 375, 400, 425, 440, 455, 470, 490, 500, 510, 520, 530, 540, 550, 575, 580, 600, and 625 mμ. The values of absorbancy are required although on many instruments it may be desirable to read $\%T$ and convert these for plotting. The spectra for the 0.0752 M cobalt and for the 0.0200 M chromium solutions are plotted on one graph. A curve representing the graphical



Curve A, 0.0752 M cobalt(II) nitrate; curve B, 0.0200 M chromium(III) nitrate; curve C, curve only—the sum of A and B points—experimental points for the mixture.

sum of these two spectra is then drawn. Finally the experimental values for the mixture are plotted and, if the measurements have been carefully made, these points will fall closely on the graphical sum of the other spectra. This fact shows that the linearity relationship holds. (Though strictly this is only demonstrated for a mixture of this particular composition, this is usually taken as being sufficient.)

It is now seen that the cobalt spectrum has a reasonably flat maximum near 510 mμ and that the chromium spectrum has one near 575 mμ which may be used for analysis. These wavelengths will hereinafter be referred to as λ_1 and λ_2, respectively.

"Beer's Law Plots" and the Evaluation of the k_{ij}'s. Plots of the absorbancy as a function of concentration (A versus C) are now obtained for cobalt and for chromium both at λ_1 and λ_2. The stock solutions are included in these measurements. The slopes of the straight lines obtained are evaluated graphically to obtain the values of the k_{ij}'s. Inspection of equations (2) shows that the slope of the line for cobalt (component 1) measured at λ_1 is just equal to k_{11}, and the slope at λ_2 is k_{21}, whereas k_{12} and k_{22} are obtained similarly from the plots for chromium at λ_1 and λ_2, respectively. It is true that these constants might be calculated from single experimental measurements, but their evaluation from the slopes is more accurate.

Analysis of Unknowns and Calculations. It only remains to measure the absorbancy of the unknown solutions at λ_1 and λ_2, and the desired concentrations may be calculated. If we solve equations (2) for the concentrations, we obtain

$$\begin{aligned} c_1 &= p_{11}A_1 + p_{12}A_2 \\ c_2 &= p_{21}A_1 + p_{22}A_2 \end{aligned} \qquad (3)$$

where

$$p_{11} = \frac{k_{22}}{k_{11}k_{22} - k_{12}k_{21}} \qquad p_{12} = \frac{-k_{12}}{k_{11}k_{22} - k_{12}k_{21}}$$

$$p_{21} = \frac{-k_{21}}{k_{11}k_{22} - k_{12}k_{21}} \qquad p_{22} = \frac{k_{11}}{k_{11}k_{22} - k_{12}k_{21}}$$

Thus, once the p's are obtained from the experimental values of the k's, one has direct equations from the c's with known coefficients. The use of matrix methods in obtaining solutions such as these may be described to the student and the near-necessity for such methods pointed out in cases such as multi-component infrared analysis (*4*) and mass spectrometry (*5*) where the number of components, and equations, may be as large as ten to twenty.

Results

Results obtained by one of the authors (J. T. M.) using a Bausch and Lomb "Spectronic 20" spectrophotometer with the standard round cuvettes supplied are given in Table 1. Absorption spectra obtained are displayed in the figure.

$$p_{11} = 0.155_{p12} = -0.096_{p21} = -0.0110_{p22} = 0.060_2$$

Table 1

Substance	Taken (moles/liter)	Found (moles/liter)	% Error
Cobalt	0.0673	0.0675	0.3
Chromium	0.0179	0.0180	0.6

Students were issued unknowns, consisting of accurately measured volumes of the stock solutions delivered into 25-ml glass stoppered volumetric flasks, yielding on dilution easily calculated apparent concentrations, unaffected by any small errors in the real concentrations of the stock solutions. A summary of the results for 70 analyses obtained by students, also using the "Spectronic 20" is given in Table 2.

Table 2[a]

	Number of Results with error in range					
	0–2	0–4	4–6	6–3	8–10	>10
Cobalt	15	7	12	5	6	25
Chromium	24	13	9	9	2	13

[a] Limits of concentration given: cobalt 0.0400 M to 0.1300 M; chromium 0.0075 M to 0.0200 M.

Of the 25 cobalt analyses with relative error greater than 10%, there were 14 where the molar ratio of cobalt to chromium was less than 3.5; and of the 13 chromium analyses with similar relative error, 9 contained a molar ratio of cobalt to chromium greater than 8. This gives indication of the reasonable limits of concentration ratios for unknowns. With the equipment used it was found to be important to use great care in aligning the cuvettes and to make repeated readings to insure accuracy of 0 and 100% reference settings.

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Many times a day I realize how much my own outer and inner life is built upon the labors of my fellow-men, both living and dead, and how earnestly I must exert myself in order to give in return as much as I have received. My peace of mind is often troubled by the depressing sense that I have borrowed too heavily from the work of other men.

Albert Einstein

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The Measurement of Properties in Physical Chemistry

Some physical properties of liquid organic compounds are commonly studied in the first semester of laboratory work in physical chemistry. Many instructors have sought devices to give these experiments added interest and importance to students; the use of unknown liquids is commonly suggested in laboratory manuals, and Slowinski (*1*) has suggested that each student perform all his determinations upon a single unknown, thus creating a unity of purpose for the entire series. The present paper describes an experimental approach to the study of the usual physical properties which offers the desirable features of an unknown, and in addition the challenge of acquiring new data for correlation and interpretation.

For his study of the physical properties each student is given 150 ml of a pure unknown liquid, from which he prepares three different benzene solutions of accurately known composition. Measurements of the specific gravity, viscosity, surface tension, and refractive index of these solutions, pure benzene, and pure unknown are made at constant temperature. In addition, the variations of these properties of the pure unknown and of benzene with temperature are determined. The student can then plot the variation of each property as a function of solution composition at one temperature, and also as a function of temperature for the pure material as compared to benzene. He then determines the boiling point and molecular weight (freezing point method) of his unknown; the unknown is identified from the data at hand, which together with the correct molecular weight are used for all subsequent calculations.

A rough value for the critical temperature of the unknown is obtained from the boiling point, and also by extrapolating the surface tension curve to the T-axis (*2*). Molar refraction and parachor values are calculated and compared with the sums of the corresponding atomic and group values; the independence from temperature of these quantities is checked. The student is asked to compare his experimental values with those in the literature; he may be surprised at how few can be found. He should also discuss the ideality of his solutions and consider his results in terms of additive, constitutive, and colligative properties.

There are many empirical relationships and equations which may be profitably investigated with the information gleaned from these experiments. It is stated (*3*, *4*, *5*) that fluidity varies linearly with composition for an ideal solution. Log viscosity may be plotted versus $1/T$ (*3*). A rise in temperature of 0.1° is said to cause a 0.2% decrease in viscosity (*5*). It has also been said (*4*) that a viscosity-composition curve usually sags, unless there is compound formation. Refractive index is described as decreasing by 0.0004 units per degree rise in temperature (*6*).

For optional work a student may check the statement (*7*) that the refractive index of a solution equals the sum of the mole fraction times refractive index terms for each component. He could also calculate the partial molal volume of his solution (*8*). He might be asked to plot $(M/d)^{1/3}$ versus T, and to obtain the slope of the resulting straight line. This slope may be compared with the Eotvos constant $k = 2.12$, and the association factor $x = (2.12/k)^{1/3}$ can be found. If desired, T_c may be obtained from the Ramsey-Shields equation (*9*). In many cases an accurate value of T_c can be calculated from the boiling point, as described by Marschner and Beverly (*10*). These are but a few of the relationships which have been proposed (*11*).

Liquids suitable for use as unknowns must meet the requirements of miscibility with benzene, low melting point, non-association in solution, commercial availability, and reasonable purity. For best results with the isoteniscope, the unknown's normal boiling point should not be above 160°C (*12*). For viscosity studies it is recommended (*4*, *5*) that the viscosities of the unknown and of the solvent differ by not more than a factor of three. A survey of the Eastman Organic Chemicals List No. 41 resulted in the following group of compounds, unusual enough to be interesting, possessing the desired properties, and in most cases tested in the course at Hamilton. All are of "white label" purity, assumed satisfactory for use without further purification, and less than five dollars per five hundred grams in cost.

2-Butanone
n-Butyl ether
p-*t*-Butyltoluene
1-Chlorobutane
1,4-Dichlorobutane
Diethyl carbonate
Dimethoxymethane
N,*N*-Dimethylformamide
Epichlorhydrin
Ethylbenzene
Ethyl formate
n-Heptane
2-Heptanone
n-Hexyl ether
Methyl benzoate
3-Methyl-2-butanone
4-Methyl-2-pentanone
α-Methylstyrene
o-Nitrotoluene
3-Pentanone
Triethyl orthoformate
2,2,4-Trimethylpentane

With regard to the accuracy of the various physical methods, the molecular weight determination has been found the poorest in practice, results being accepted if within two per cent of the correct value. Specific

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gravity values should be accurate to within 0.2% using the Westphal balance, viscosity, and surface tension to within 0.5% by the Ostwald viscometer and capillary rise methods, respectively, and refractive index to within 0.05%. For such accuracy and good precision, careful temperature control is essential, indicating the use of a tenth-degree thermometer. One desirable feature of these experiments is the graphic demonstration of the need for careful control of experimental conditions; it has been observed that the students soon treat such matters spontaneously in the most effective way, by use of large volume baths, etc., and carry over the principles to subsequent experiments without urging.

Experience since 1955 with the program just described has shown it to be most fruitful. The better students are fascinated by the interrelationships made apparent, and by finding themselves on the borderline between theoretical knowledge and empirical guesswork. All appreciate the unity and sense of accomplishment in accumulating a store of facts about one compound. It is even possible that an edited collection of many such results could usefully contribute to the permanent body of physical knowledge.

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A Safe Method for Preparation of Uncontaminated Hydrazoic Acid

H. S. Booth's "Inorganic Synthesis"[1] reports that hydrogen azide can be prepared by the reaction of strong sulfuric acid (40 per cent) upon a sodium azide solution containing sodium hydroxide. Sodium hydroxide is used as a moderator of the reaction since hydrazoic acid vapor in high concentrations is spontaneously explosive. In the procedure, the solution of sodium azide and sodium hydroxide contained in a flask connected through a condenser is brought to boiling and the acid is added to the hot boiling solution.

During efforts to make pure aqueous solutions of hydrazoic acid in connection with the preparation of some pure alkali metallic azides it was observed that during the precipitation and crystallization of potassium azide small amounts of potassium sulfate were always present. Potassium sulfate is less soluble in water than potassium azide, and during attempts to grow potassium azide single tetragonal crystals, the orthorhombic sulfate form was always present.

Sulfuric acid in the presence of its salts or more volatile acids tends to fume at temperatures much below the boiling point, or at about 160°C. During the addition of the sulfuric acid to the boiling solution in this procedure, it is obvious that the exothermic reaction between the strong sulfuric acid and the solution causes premature decomposition of the sulfuric acid, and fumes carried into the receiving flask are subsequently transformed, in this case to potassium sulfate.

In an effort to eliminate the sulfate contamination this laboratory has modified the procedures somewhat. The same reagents are used as the source of the hydrazoic acid. The procedure is as follows: A saturated solution of sodium azide is placed in the round bottom flask and a stream of nitrogen is allowed to flow through for at least thirty minutes. One and $\frac{1}{10}$ times the required stoichiometric amount of sulfuric acid is added dropwise, cold, and the mixture heated slowly to boiling and boiled 5 to 10 minutes. The evolved hydrazoic acid is received in a flask surrounded with an ice bath. The yield is almost quantitative, and any dilutions desired in the prepared hydrazoic acid solution are made by adding water to the receiving flask. Nitrogen is allowed to flow through the system during the entire run although during the boiling it could be dispensed with. In 40 to 50 preparations of hydrazoic acid not once did any explosions occur although solutions 75 to 80 per cent in hydrazoic acid were often prepared.

This modification of the procedure eliminates the hazard of high concentrations of hydrazoic acid in the vapor phase and also yields a product free of the sulfate impurity.

[1] Audrieth, L. F., and Gibbs, C. F., *Inorganic Synthesis*, McGraw-Hill Book Company, New York, **1939**, Vol. 1, p. 77.

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A Laboratory Study of Liquid Pairs

Often the effectiveness of the physical chemistry laboratory is impaired by the boredom of uninteresting experiments. It is difficult to inspire the student to train himself in necessary and valuable skills if the apparent experimental goal is to duplicate accepted physical constants which can be found with greater ease and accuracy in the chemical literature than in the laboratory. Of the many experiments which may emerge as deadening routine, a conspicuous example is the measurement of liquid properties, e.g., surface tension and viscosity. These determinations can easily become mechanical and uninspiring. Two changes in these experiments have served to convert an unpopular chore into a more interesting search: (1) the use of unknowns in the form of miscible liquid pairs, and (2) the combination of several traditional procedures into a single extensive discovery experience.

The study of properties of liquids takes up the second month of laboratory work. Students work in pairs as the use of instruments is rotated in the class. Two students working together gain much from discussion of their mutual problem. They are issued two miscible liquids bearing a code label. In about four or five afternoons they complete the following experiments: (*a*) make up a series of solutions by weight per cent and determine their densities with a Westphal balance: (*b*) determine viscosity coefficients using an Ostwald viscosimeter; (*c*) find the surface tensions by capillary rise; (*d*) measure refractive indices with an Abbé refractometer; (*e*) by incremental addition of liquids determine the boiling points of liquid mixtures whose compositions of liquid and vapor are found from refractive index measurements. Several traditional experiments are thus combined into a single large investigation of the physical properties of a liquid mixture. Identification of the liquids from their physical constants follows as a relatively simple matter, and the solution data are graphed as functions of concentrations recalculated as mole per cent. As much as possible the curves in the report are superposed on a single graph in order to relate different properties at given concentrations. Surface tension and viscosity provide particularly interesting comparisons.

The liquid pair study is reported as one investigation rather than as a group of experiments. The report includes extensive discussion in addition to a brief description of procedure, data tables, and graphs. Students are provided with directions for the experiment, including a few leading questions to guide the discussion and point up applications. In particular, the student is led to observe and to seek explanation for such anomalies as viscosity maxima and azeotropic mixtures. He is expected to interpret the vapor composition diagram and to apply it to hypothetical situations such as predicting composition changes during a given temperature interval. The use of unknown liquids, though delaying liquid identification only until a few measurements can be made, does make the student cognizant of the need for accurate data for identification purposes and thus keeps up interest in the experiment. Results of many other liquid pair studies are posted in the laboratory and the students are expected to make comparisons and seek correlations between the properties of the solutions and those characteristics of the component.

The students turn in duplicates of their graphs for filing so that results may be compiled from year to year. Some examples taken from these experiments are as follows:

Surface Tension. Carbon tetrachloride in butanol—linear and little change. Heptane in benzene—slight negative deviation from ideal. Methyl acetate in isopropyl ether—pronounced curve minimum.

Viscosity. Methanol in water gives a pronounced maximum. Carbon tetrachloride in carbon disulfide—nearly linear. Heptane in benzene—negative deviation.

Distillation. Chloroform in ethyl acetate—azeotropic mixture with maximum. Chloroform in methanol—minimum azeotrope with very wide branching.

Composite graphs showing all three of the above properties versus composition show linear viscosity and surface tension variation and widely separated liquid-vapor curves for xylene-benzene. Negative viscosity deviation, linear surface tension, and minimum azeotrope are seen in the graphs for carbon disulfide-acetone. Methanol-chloroform give positive deviation in viscosity and surface tension and a well-spread liquid-vapor graph with minimum boiling point. In the large number of other combinations of liquids that can be used, interesting and sometimes unexpected behavior is noted.

The liquid pair study does not preclude the inclusion of other usual measurements in the experiment. The viscosimeter and surface tension capillary are calibrated in the customary manner. A series of polymer solutions can be provided for determination of intrinsic viscosity. Evaluation of specific and molar refractions, and from them the atomic and group refractions, is usually a part of the experiment, as is also the use of an immersion refractometer for analysis of salt solutions. Many of the students are concurrently taking the course in qualitative organic analysis; for them the liquid pair study serves to strike a parallel between chemical and physical methods of identification.

Presented before the Division of Chemical Education at the 136th National Meeting of the American Chemical Society at Atlantic City, September, 1959.

The use of unknowns has provided a great deal more interest in the laboratory measurements. The occurrence of unexpected trends and changes serves to keep the student watchful lest he overlook significant data; sometimes critical regions suggest repetition of measurement for greater clarity of results. The experiment affords good opportunity to stress accuracy and precision of measurement without making it a burdensome chore. Effective presentation of the data calls for proper selection of scales and good graphing technique. The student is expected to draw conclusions and interpretations from this data, to make specific applications, and to correlate his findings with theory. Finally, and not of least importance, the experiment takes on the aspect of an exercise in research rather than a routine recording of disconnected physical measurements.

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Tie Line Correlation and Plait Point Determination

An experiment on phase equilibria in a heterogeneous ternary liquid system is frequently assigned in the laboratory in elementary physical chemistry. As presently constituted in the current laboratory texts, the experiment consists only of the determination of the binodal curve and several tie-lines. It is possible, however, using only the data taken for the above purpose, to make this a more informative experiment by utilizing tie-line behavior to determine the plait point. The method is one of those commonly followed in research, where a direct determination of the plait point appears to be a rarity.

A number of approaches for tie-line correlation have been proposed (*1–7*). Of these, all but two, those of Bachman and Dryden, are of forms less desirable for work at the elementary level. The method selected for this experiment was that of Bachman. The Bachman equation may be expressed in the form $a_1 = m\,(a_1/b_1) + k$, where a_1 is the per cent by weight of one of the non-consolute liquids (A) in the phase richer in that component, b_2 is the per cent by weight of the other non-consolute liquid (B) in the corresponding conjugate phase in which it is richer, and both m and k are empirical parameters. Frequently it is found that m and k are constant for an isothermal system; the equation is then obviously that of a straight line. This is generally found to be so when the two non-consolute liquids are markedly insoluble. The equation was first developed empirically, but it has been shown (*5*) to bear a resemblance to the familiar Nernst distribution equation.

The basic experiment to which the work described in this paper was appended is described in a current laboratory text (*8*). The system studied was acetic acid-benzene-water, although a number of other systems found in different texts would be equally suitable.

Figure 1 illustrates the nature of the phase diagram of the system studied. The binodal curve and tie-lines represent the accepted values at 25°C (*2*). The individual points on the diagram are those determined by the students in this laboratory. They have been included to give an indication of how the accuracy in determining the plait point depends upon the accuracy in determining the solubility curve. The tie-lines determined by the students are not included here, since their accuracy is indicated in Figure 2 below. The experiment was performed at room temperature, which varied from about 23–7°C.

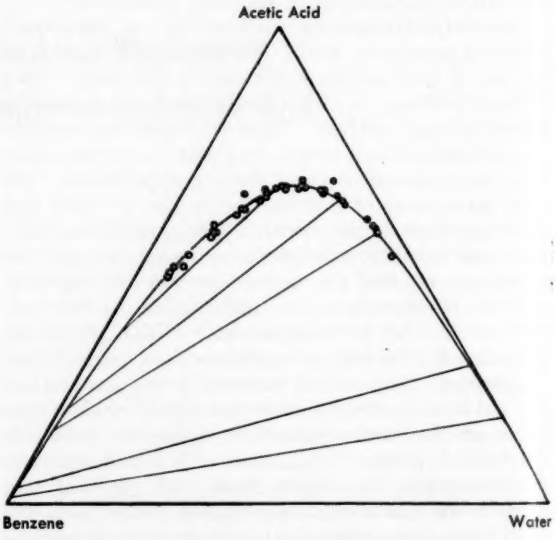

Figure 1. The system acetic acid-benzene-water.

The tie-line correlation plot used in estimating the plait point is given in Figure 2, where A represents water, and B benzene. The solid line is the relationship obtained by the use of the accepted values. Included in the figure, also, are the points obtained by the students, which indicate the spread in data to be expected. The laboratory text directs that four tie-lines be obtained. Several students had a single bad point, but in each instance their other three points gave a well-defined straight line.

Presented before the 15th Southwest Regional Meeting of the American Chemical Society, Baton Rouge, December, 1959.

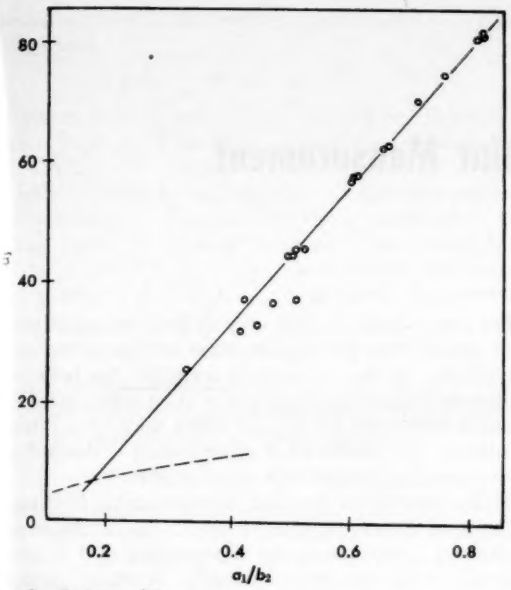

Figure 2. Bachman plot.

The plait point is determined by the intersection of the plot of the Bachman equation with the dashed line near the base in Figure 2. The latter line is established from the solubility curve and represents a locus of points upon which the plait point must lie. It is obtained by estimating possible locations of the plait point, which may be roughly fixed by the general trend of the tie-lines in the phase diagram. Values of a and b at the various estimated plait points are recorded. Since each point is tentatively assumed to be the plait point, for each of these points $a = a_1$, and $a/b = a_1/b_1 = a_1/b_2$, for the two conjugate phases become identical at the plait point. As the plait point must also lie on the extension of the line representing the Bachman equation, the intersection of the two lines defines the plait point. The dashed line used to illustrate this relationship in Figure 2 was drawn using the accepted values.

From individual plots of student data the values of a at the plait point were found to be 7.0, 7.2, 7.5, 7.5, and 8.5. The accepted value is 7.2, indicating a satisfactory agreement for the purpose intended. The reaction of the students toward this additional aspect of the experiment was favorable. They were interested to learn that there is a systematic relationship between the tie-lines which may be used both for interpolation purposes and for location of the plait point.

It appears that the determination of an additional tie-line nearer the plait point might reduce the uncertainty in the required extrapolation of the Bachman plot.

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Seven Precepts of the Student Laboratory

Original Form	*Translation*
1. Horseplay belongs in a corral.	1. You don't get a second chance to grow an eye.
2. Clean equipment ⟶ better results.	2. The soap industry didn't reach its present size because its products weren't useful.
3. You can't use equipment from your desk unless you can find it.	3. $C_s \propto O_d$; $\frac{1}{F_b} \propto O_d$ where O_d = desk orderliness, C_s = speed of completing lab work, F_b = breakage fines
4. If you need a chemical from the stock shelf, "Take Mohammed to the Mountain."	4. 99.47 (±0.04%) of all laboratory motion follows the question, "Who took the silver bromide?"
5. If the stock bottle is low—TATTLE!	5. Your neighbor may be slower than you, but he'll need some pretty soon. . .besides you need another 20 g for proc. 6(*b*).
6. "...in case of accident. ." Rules are not legal statutes, therefore you can follow them without infringing on your legal rights as a citizen.	6. Acid, spilled on the skin, *is not* neutralized by oil of vitriol.
7. Many previous chemists have had their surface anatomy altered so that *you* could *read* what to do.	7. The lab book *did not* say, ". . .add 10 ml water to 25 g sodium metal in a small beaker."

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Freezing Point Measurement

Measurements of the molal freezing point depression of solutions containing a nonvolatile solute may be used to determine molecular weights and activity coefficients. This requires that the freezing points of the pure solvent and of the solution be measured. This is usually carried out by placing the solution in a double-walled vessel which is immersed in a freezing mixture contained in a wide-mouthed Dewar flask. By means of a differential thermometer the lowering of the freezing point from that of the pure liquid by the addition of a nonvolatile solute is determined.

The freezing point values are determined from the cooling curves obtained by recording the temperature as a function of time. The ideal curve is shown in Figure 1 as curve A. The temperature at the plateau on the curve is recorded as the true freezing point, $T_f°$.

However, the more common type of cooling curve is shown in Figure 1 as curve B in which the temperature continues to fall beyond $T_f°$. This is known as supercooling. When the solid phase nucleates, the latent heat of fusion is liberated to the surroundings and the curve rises. Finally heat is drawn from the solid mass and the cooling curve falls once more. Since the maximum value, T_f, recorded at the top of the sigmoid curve B does not equal $T_f°$, supercooling is an undesirable phenomenon and attempts are usually made to minimize it.

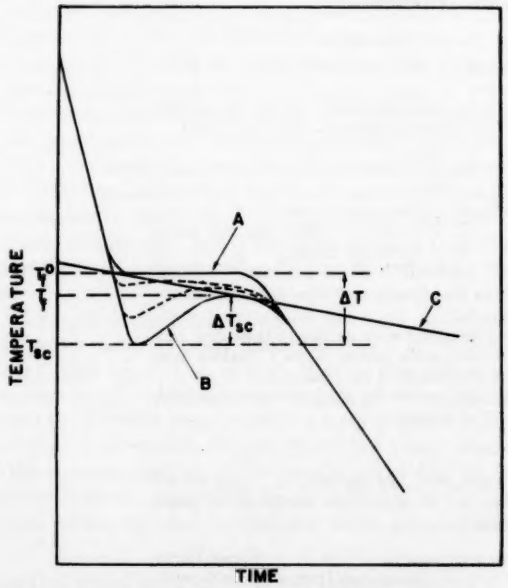

Figure 1. Cooling curves: *A*, without, and *B*, with, supercooling.

For some solutions, it is very difficult to separate the solid phase from the liquid phase and supercooling is inevitable. At this laboratory, a method has been used to measure the freezing points of such solutions which seems to give good results and which may be of interest to others. In this method supercooling is desired and encouraged under a definite set of conditions.

A dry ice-acetone freezing mixture and a Beckmann differential thermometer were used. To minimize concentration errors due to the supercooling and to insure constant heat transfer, a steady, constant, vertical stirring was obtained by connecting the ordinary looped stirring rod to an automobile windshield-wiper motor.

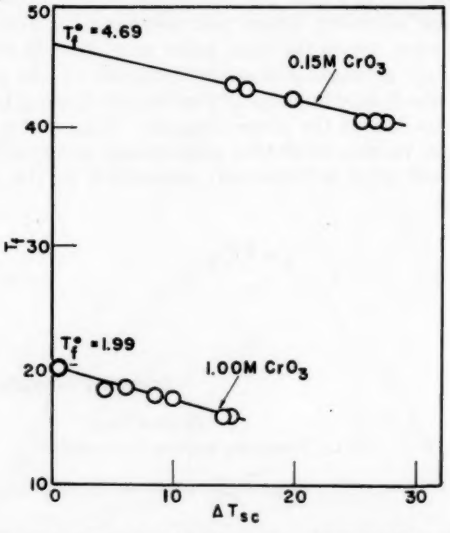

Figure 2. Plots of T_f against ΔT_{sc} for solutions of CrO_3 in 1.79 M H_2SO_4 in water.

The minimum temperature, T_{sc}, and the maximum temperature, T_f (See Fig. 1), were recorded and a plot of $(T_f - T_{sc}) = \Delta T_{sc}$ against T_f was made. It is seen from Figure 2 that such a plot gives a straight line, the slope of which is determined by the thermal properties of the system. The curves shown in Figure 2 were obtained from measurements made on solutions of 0.15 M and 1.00 M CrO_3 in 1.79 M H_2SO_4 in water. The Beckmann thermometer was set with reference to 1.79 M H_2SO_4 in water. The intercepts at $\Delta T_{sc} = 0$ are recorded as the freezing points, $T_f°$, of these solutions.

In order to find what conditions must be met to obtain the type of curves described in Figure 2, one may consider the heat transfer relationships involved. In the system described here, the rate of loss of heat from

the test solution to the cooling reservoir at $T_f°$ is given by v_L, where

$$v_L = Kf(r)\,(T_f° - T_b)$$

and where K is an overall heat transfer coefficient and $f(r)$ is a function of the dimensions of the system and of the stirring rate. Both of these quantities are essentially constant for a given series of measurements on a given solution. Finally, T_b is the temperature of the cooling bath. A freezing mixture is so chosen that $(T_f° - T_b) \gg (T_f° - T_{sc})$. Then within the supercooling range $T_f° > T > T_{sc}$, v_L is essentially constant since

$$(T_f° - T_b) \simeq (T_{sc} - T_b)$$

When the system has supercooled and the solid phase has begun to separate, the latent heat of fusion is liberated to the surroundings at a rate equal to

$$v_G = K'f(r')\,(T_f° - T_{sc}) = \text{const}\,(\Delta T)$$

where the primes indicate that the parameters associated with v_G may not be the same as those associated with v_L. The smaller ΔT is, the lower v_G is. Consequently, the rise of curve B after initiation of the solid phase becomes less steep as shown by the dotted curves in Figure 1. Although the maximum value, T_f, is increased, $T_f°$ is not reached because v_L is so large that its influence is rapidly felt and the curve begins to turn downward. The overall rate of gain of heat after initiation of the solid phase is $v = v_G - v_L$. Since $v_L = \text{const}$, $v_G = \text{const}\,(T_f° - T_{sc})$ and $T_f°$ is a constant, $v = f(T_{sc})$. ΔT_{sc} and the maximum temperature reached, T_f, are functions of v_G. Then, $T_f = f(\Delta T_{sc})$. It may be seen from Figure 2 that this function is linear. This means that the shape of the B-curves in Figure 1 are such that a straight line drawn through the maximum points, T_f, cuts the B curve at $T_f°$ as shown by the curve, C, in Figure 1. $T_f \rightarrow T_f°$ as $\Delta T_{sc} \rightarrow 0$. $T_f = T_f°$ only when $\Delta T_{sc} = 0$; that is, only in the absence of supercooling. When supercooling is present, $T_f \neq T_f°$. However, supercooling may be minimized in many cases to the point where $T_f° - T_f$ is negligible. It is seen, then, in cases where the supercooling is ever-present, one may obtain good approximations to the freezing points by the deliberate use of supercooling. Two important conditions to be met are: a low temperature freezing mixture, $(T_f° - T_b) \gg (T_{sc} - T_b)$, and good constant stirring to insure constant heat transfer. The equation for the curves in Figure 2 is

$$T_f = k\Delta T_{sc} + T_f°$$

An obvious error involved is due to the concentration changes incurred as the solid phase separates from the liquid. This tends to give a value too high for the freezing point depression.

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Estimating Standard Oxidation Potentials

A relation between the electrode potentials and the oxidation potentials of an element in various oxidation states has been proposed by Luther and Wilson (*1*). It is developed as follows:

Let the following equilibria between the various oxidation states of an element be:

$$\begin{aligned} M^{a+} &\rightleftharpoons M^{b+} + (b-a)e^- \quad \ldots E°_{a/b} \\ M^{b+} &\rightleftharpoons M^{c+} + (c-b)e^- \quad \ldots E°_{b/c} \\ M^{a+} &\rightleftharpoons M^{c+} + (c-a)e^- \quad \ldots E°_{a/c} \end{aligned}$$

In isothermal-isobaric reversible processes the work done depends only on the initial and final states. For $\Delta F°$, the free energy change, we have:

$$\Delta F°_{a/c} = \Delta F°_{a/b} + \Delta F°_{b/c}$$

since

$$\Delta F° = -n\mathfrak{F}E°,$$
$$(c-a)E°_{a/c} = (b-a)E°_{a/b} + (c-b)E°_{b/c}$$

or

$$E°_{a/c} = \frac{(b-a)E°_{a/b} + (c-b)E°_{b/c}}{c-a}$$

By means of this formula, when two standard oxidation potentials are known, the third related potential value can be estimated. The difficulty in the application of this rule is that in general the related potential values are not available. Further it may be that the potentials and free energy data, respectively, are not consistent with the known ones. Perhaps this is why the Luther-Wilson rule is so infrequently applied.

The difficulty which arises from the lack of the related potential values and from the inconsistency of some data can be eliminated when the required value is estimated by means of the following function:

$$E°_i = f(\Sigma n_i)$$

It can be shown from available consistent data that when the various standard potential values of an element are plotted against the sum of the oxidation numbers of the species which take part in the equilibria, straight lines are obtained. (See the figure for typical data so treated.) The plotting for the order of the individual potential values gives the same result as that obtained from the Luther-Wilson rule. When the

successive oxidation states are designated a, b, and c (i.e., $a < b < c$), then the value of the standard oxidation potential of the a/c transfer always lies between the potential values of a/b and b/c transfers, i.e.,

$$E^\circ_{a/b} < E^\circ_{a/c} < E^\circ_{b/c}$$

or

$$E^\circ_{a/b} > E^\circ_{a/c} > E^\circ_{b/c}$$

It can be easily proved that the above function yields the Luther-Wilson relation. Let k, l, and m represent the sum of the oxidation numbers of the species taking part in the corresponding couples:

$$k = a + b,\ l = a + c,\ \text{and}\ m = b + c.$$

According to the linear function (Fig. 1) obtained we can write:

$$\frac{E^\circ_{b/c} - E^\circ_{a/b}}{E^\circ_{a/c} - E^\circ_{a/b}} = \frac{m - k}{l - k}$$

and substituting the values of k, l, m, and reducing we get the Luther-Wilson rule:

$$(c - a)E^\circ_{a/c} = (c - b)E^\circ_{b/c} + (b - a)E^\circ_{a/b}$$

For the applicability of the function given, the following example is illustrative: Calculate the standard oxidation potentials of the various species obtained by the reduction of chromic acid, i.e., the values of $E^\circ_{3/4}$, $E^\circ_{3/5}$, $E^\circ_{4/5}$, $E^\circ_{4/6}$. Since only $E^\circ_{3/6}$ and from Westheimer's estimation (*2*) $E^\circ_{5/6}$ are known ($E^\circ_{5/6} = -0.60$ volt), direct calculations cannot be performed.

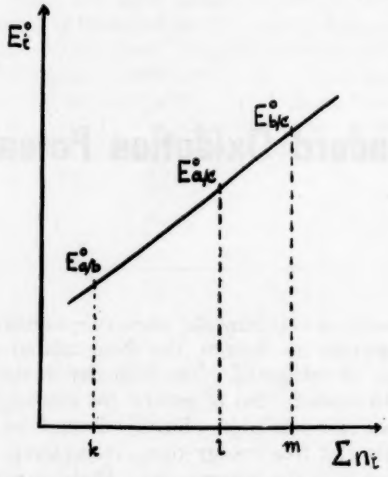


Figure 1. Estimation of oxidation potentials.

But on the basis of the Luther-Wilson rule the following relations exist between the potentials:

$$3E^\circ_{3/6} = E^\circ_{3/4} + E^\circ_{4/5} + E^\circ_{5/6} = 2E^\circ_{3/5} + E^\circ_{5/6} = E^\circ_{3/4} + 2E^\circ_{4/6}$$

and from this it follows that upon plotting the function

$$E^\circ_i = f(\Sigma n_i)$$

the values of $E^\circ_{3/4}$, $E^\circ_{3/5}$, $E^\circ_{3/6}$, $E^\circ_{4/5}$, $E^\circ_{4/6}$, and $E^\circ_{5/6}$ lie on a straight line. From this straight line determined by the two known points, the required values can be estimated.

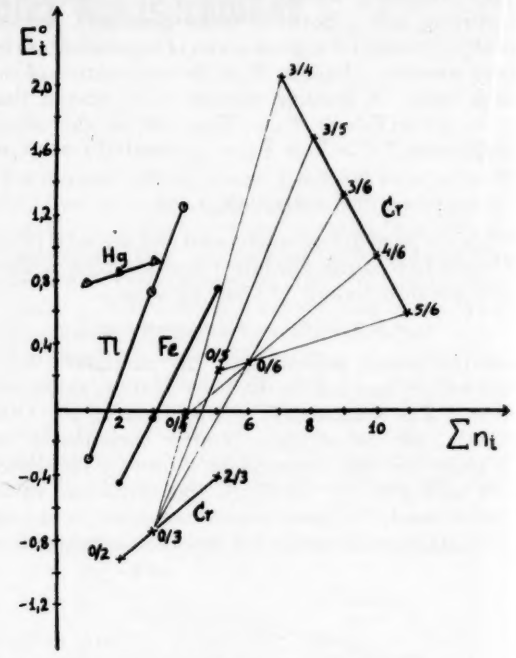


Figure 2. Some examples of plotting E°_i as a function of Σn_i.

The potential values obtained are the following:

$E^\circ_{3/4} = -2.10$ volts $E^\circ_{4/5} = -1.345$ volts
$E^\circ_{3/5} = -1.72$ volts $E^\circ_{4/6} = -0.97$ volt

The computed values of free energy of formation of the species of Cr(IV) and Cr(V) are:

$Cr(OH)^{3+}$ aq: -59.68 kcal
$HCrO_4^{2-}$ aq: -198.74 kcal

Besides the estimation of unknown potential values the $E^\circ_i = f(\Sigma n_i)$ function can be applied for evaluating the consistency of tabulated data. For example, plotting the function above we had observed that for the transfer

$$Sb_2O_3 + 2H_2O = Sb_2O_5 + 4H^+ + 4e^-$$

the value $E^\circ = -0.692$ is incorrect (*3*). The correct value is $E^\circ = -0.670$ volt.

Thanks are due to Prof. Dr. Z. G. Szabó and Dr. P. Huhn for valuable discussions.

Literature Cited

(1) Luther, R., and Wilson, D. R., *Z. Physik. Chem.*, **34**, 488 (1900), and *ibid.*, **36**, 385 (1902).
(2) Westheimer, F. H., *Chem. Revs.*, **45**, 419 (1949).
(3) Latimer, W. M., "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall Inc., New York, 1952, p. 119.

Joseph A. Feighan
Saint Joseph's College
Philadelphia, Pennsylvania

Measurement of Vapor Pressure

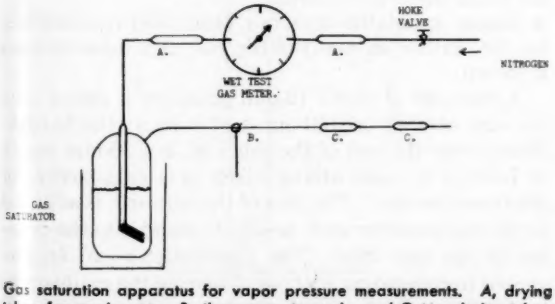
A gas saturation method

Although most elementary and advanced texts in physical chemistry give the theoretical discussion of the measurement of the vapor pressure of liquids by gas saturation methods, there is a noticeable absence of experimental procedures in the current laboratory texts. This experiment is appropriate for teaching experimental techniques and can give satisfactory results in the hands of the typical undergraduate physical chemistry student in a three-hour session.

The Experiment. The apparatus as used is shown in the figure. Tank nitrogen was metered slowly through a wet test gas meter at a known temperature to measure its volume and then dried upon exit to remove water that was vaporized in the meter. The flow of gas was controlled by a Hoke needle valve and could be varied to cover a range of flow rates.

The exit gas was directed into a saturator (sintered glass type gas dispersion unit) containing the liquid under study, and the gas bubbles allowed to escape, and then was directed into a bypass by means of a three-way stopcock, *B*. After thoroughly saturating the tubing in the system with the vapor of the liquid to be measured, the stopcock was turned and the vapors directed into a collection system, *C*.

The method of collection of vapors was of two types. Either a solid desiccant, in previously weighed drying tubes was used for materials such as water, alcohols, or amines, or a cold trap for materials more difficult to remove by adsorption. The exit nitrogen, freed of its vapors, was passed out through the drying tubes, *C*.



Gas saturation apparatus for vapor pressure measurements. *A*, drying tubes for carrier gas; *B*, three-way stopcock; and *C*, two drying tubes, containing solid adsorbent, suitable for adsorption of vapor under study.

Calculations of the vapor pressure were carried out by use of the ideal gas law in cases where the volume of vapor was negligible compared with the volume of inert gas.

The more accurate equation,

$$p_v = \left(\frac{n_v}{n_v + n_g}\right) P_t$$

where

p_v = vapor pressure of liquid under study
n_v = number of moles of liquid adsorbed
n_g = number of moles of carrier gas used as inert gas sweep and,
P_t = barometric pressure

is used where the volume of vapor carried over is appreciable when compared with the volume of carrier gas used.

Under carefully established conditions, it has been possible to obtain results showing 1–2% deviation from accepted values for many liquids, such as water, methyl, ethyl, propyl and isopropyl alcohols, and acetone.

More important than these results, however, the method of demonstrating saturation of the carrier gas and the need for an equilibrium between carrier and vapor of the liquid being studied are seen by comparison of results at two different flow rates. The following results for water are indicative of this effect.

Flow Rate	Deviation from Literature
0.80 liter/min	3.5%
0.53 liter/min	1.5%
0.44 liter/min	3.3%
1.40 liter/min	20.5%

The vapor pressure for water showed acceptable results in the first three runs, but was far too low (20.5% deviation) on reaching a 1.40 l/min flow rate, preventing attainment of equilibrium between nitrogen and water vapor in the saturator.

Selective adsorption of gases in a mixture and the basis of the adsorption method of analysis can be emphasized by suitable choice of liquid and adsorbent. Under approximately identical conditions of flow, anhydrous $CaSO_4$ has demonstrated 10% deviation from accepted literature values for vapor pressures of water, whereas anhydrous calcium chloride as adsorbent gave approximately 1–3% deviations.

In adsorption of methyl alcohol on $CaSO_4$, with flow rates 0.31 and 0.90 l/min, 39% and 49% deviations, respectively, were obtained. When silica-gel was used as adsorbent, at 0.27, 0.71, and 1.20 l/min flow rates, results were 0.5%, 2.5%, and 5.0% deviations, respectively. The high heat of adsorption in this set of runs made it possible to conveniently follow the adsorption

Presented before the Division of Chemical Education at the 13th Meeting of the American Chemical Society, Chicago, Illinois, September, 1958.

process down the length of the drying tube.

The present studies have indicated that the experiment is satisfactorily performed at flow rates varying from 0.25 l/min to 1.5 l/min if suitable choice of gas saturator is made and if the method of removal is carefully chosen. The student accuracy is sufficient to give the student confidence in his laboratory technique, and the time of the experiment (three hours) has been found sufficient for even the slower student pairs to complete four determinations.

The method can be conveniently extended to the study of the variation of the vapor pressure with temperature and calculation of the heat of vaporization, by immersion of the saturator and connecting tubing in a constant temperature bath. The drying tubes or traps would in this case be left outside the constant temperature device without introduction of serious error. The heat of vaporization of methyl alcohol and of water were determined by this approach using temperature ranges between 15 and 25°C and gave reproducible accuracy of about 1% of literature values.

It is well to emphasize again that no claim is made that this simple apparatus will duplicate results of more elaborate types such as several saturators in series or rigid flow control that might be required in research studies of vapor pressure. The principal benefit to the student chemistry major at this point in his training is the familiarization obtained with the new apparatus and methods of the physical chemistry laboratory.

An Inexpensive Apparatus for Solubility Measurements

Robert H. Schmitt and **E. L. Grove**
University of Alabama, University, Alabama

The solubility apparatus described is simple and inexpensive to make. Most of the components are found in any chemistry laboratory.

The main part of the apparatus (see figure), is a 100-ml (other sizes may be used) polyethylene bottle. To the cap of this bottle is welded a strip of polyethylene so that the system can be suspended with a wire from a variable speed motor. When small quantities of solution are used the bottle should be weighted. This can be done conveniently by using a piece of $1^7/_8$ in. i.d. lead pipe or a few turns of lead wire slipped on or off the bottle as needed.

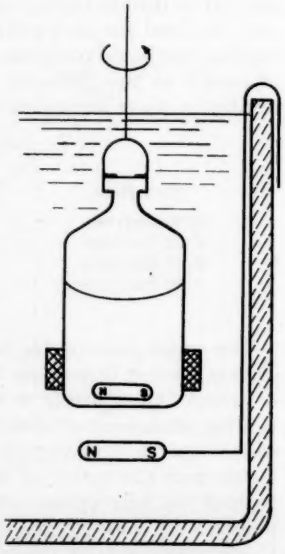
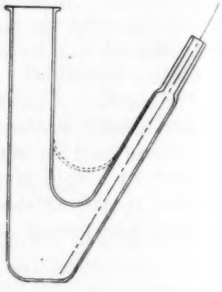


Figure 1. Cross section of solubility apparatus.

Effective stirring is accomplished by the use of an ordinary plastic-covered magnetic stirring bar in the bottle and a more powerful magnet below the bottle. It is to be noted that the bottle is rotated and the magnets are stationary. The outside magnet is held in place with #12 plastic coated copper wire, bent to cradle the magnet and to fit over the wall of the constant temperature bath.

Vessel for Small-Scale Reactions

Sidney Kasman
Polaroid Corporation
Cambridge 39, Massachusetts



It is frequently desired to conduct reactions that require close temperature control and stirring on a scale of about 0.01 to 0.03 moles. If such reactions are not carried out in dilute solution, it becomes a problem adequately to immerse a thermometer in the reaction while the reagents are being effectively stirred. A simple apparatus that has been used conveniently by the author in many nitrations and diazotizations is shown.

A side-arm of about 12-mm diameter is sealed onto the side of a 25 × 150-mm test tube at the bottom. Sealed onto the end of the side-arm is a 30-mm length of 7-mm i. d. glass tubing which acts as a sleeve for the thermometer. The axis of the side-arm is adjusted so the thermometer bulb does not extend into the cylinder of the test tube. The thermometer can be prevented from rotating without obscuring the graduations by holding it in place with 25 mm of split medium wall rubber tubing.

The capacity of the vessel can be increased by reducing the re-entrant as indicated. This does not diminish the depth of reagents bathing the thermometer when smaller volumes are employed. Additional side-arms and necks at various levels may also be sealed on the vessel as required for the addition or removal of materials.

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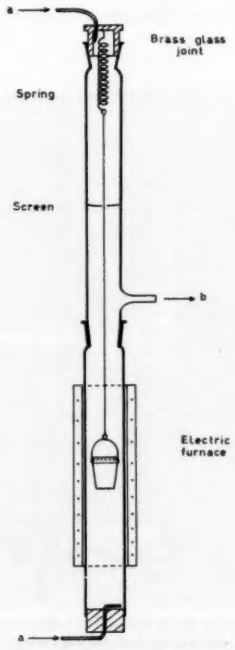
A Thermogravimetric Balance for Student Experiments

Laboratory courses in inorganic preparations often include the verification of products by analysis. In many cases, a single thermogravimetric determination may be substituted for tedious and time-consuming analyses. Such experiments also can be used to demonstrate the structure of complex compounds containing volatile or thermolabile ligands. The range of temperature over which salt hydrates are stable can be studied as well as the behavior of hydrated salts which will form basic salts on heating.

A complete treatment of the theory of thermogravimetry is available in the reference work by Duval.[1]

The accompanying figure shows schematically the essential features of a simple, robust, inexpensive homemade thermobalance. Our four years of experience with the device convince us of its utility for students' use.



Homemade thermo balance.

The spring is made from 4-mm diameter steel wire, coated with plastic to prevent rusting. It consists of 20 1-cm turns and has a sensitivity of 5 mm/g. Any desired sensitivity can be obtained easily, in a few trials, by varying the tension applied to the wire when winding it. The screen is cut out from an aluminum sheet; the screening is effective enough to allow direct calibration of the spring at room temperature. The suspension wire must be either of stainless steel or of nickel-chrome alloy.

In running the experiment, a stream of nitrogen is passed into the apparatus through the inlets (a). In the upper part, it serves to cool the spring and to prevent the introduction of water and acid vapors; in the lower one, it hinders secondary reactions with the other air components and carries away the gaseous products. If wanted, these gaseous products may be easily collected at the outlet (b) and analyzed. In other experiments, e.g., reduction or oxidation reactions, the suitable gas is substituted for nitrogen.

The stretching of the spring is read from a millimeter scale placed behind the tube. Measurement of temperature may be carried out either by means of a thermocouple, the hot junction of which is located inside the tube, or by means of a thermometer inserted in the space between the tube and the inner wall of the electric furnace. In the later instance, a systematic error as high as 30° C is to be expected; the general shape of the curve weight versus temperature, however, remains the same, as does the ordinate of the horizontal parts.

There are two important precautions to be taken in operating. Half-filling of the crucible minimizes the risk of loss of substance by "climbing" and the breaking up of small crystals on heating, and a slow but constant rate of heating is important. One degree per minute is a convenient rate, but a maximal one.

Although the theoretical accuracy of the apparatus is low, the results found in many operations are in good agreement with the calculated ones, and with those obtained with research-type apparatus as reported in the literature.

Thanks are due to Professor L. D'Or for a useful discussion of the initial design and to M. Haesen for technical help and advice.

[1] Duval, "Inorganic Thermogravimetric Analysis," New York, Elsevier Publishing Co., Inc., 1953.

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University of Tennessee
Knoxville

An Improved Victor Meyer Vapor Density Apparatus

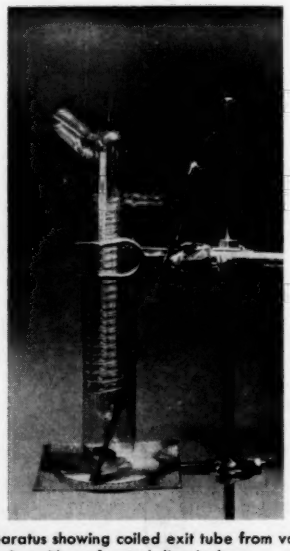
In the Victor Meyer method of determining vapor density, a weighed sample of the liquid is vaporized and the volume of air displaced from the vaporization unit is measured under the prevailing conditions of temperature and pressure in the room. The method requires a design of apparatus which will prevent the passage of the vapor from the heated vaporization unit to the unheated parts of the apparatus where condensation would take place. For this reason the vaporization unit in the ordinary form of the apparatus is made quite long. The apparatus is rather cumbersome, and it does not efficiently accomplish its purpose of retaining the vapor within the heated unit. To obtain compactness or to achieve greater security from vapor condensation, various modifications have been made.

In the Weiser[1] design, the distance the vapor must travel before escaping from the heated unit is increased by sealing a J-shaped delivery tube through the bottom of the vaporization bulb, the short end extending almost to its top and the long end extending up through the outer heating jacket. This design, which has appeared in various manuals, has two objectionable features: (1) the volume of the vaporization bulb is largely dead space which makes it necessary to insert an accessory tube to sweep out vapors between successive determinations, (2) the long leverage on the exit end of the tube makes it very susceptible to breakage at the bottom seal when assembling or disassembling the apparatus.

In the Hicks-Bruun[2] apparatus, a 10-mm tube through which the sample is introduced projects downward through a series of bulbs forming annular spaces along the seals between the bulbs. Escaping vapor or air expands successively through these small spaces giving a steady flow of air into the measuring buret. Escape of vapor from the jacketed part of the apparatus, although favored by the turbulence of flow through the small annular spaces, is prevented by the large capacity of the bulbs which total approximately 1 liter. The Hicks-Bruun apparatus was designed for a special study of the molecular weight of petroleum constituents by the method of limiting density.

In the MacInnes and Kreiling[3] design, which is conveniently homemade, compactness is achieved by means of a central vaporization tube with open lower end extending down into and almost to the bottom of the inner, jacketed compartment. The sample bulb is fastened at the top of this central tube so that when the sample bulb is crushed vapor must pass downward through the central tube, then upward around it to the top before reaching the unjacketed part of the apparatus.

The design of the Victor Meyer apparatus described here is shown in the photograph. The jacketed exit tube from the vaporization chamber is 2 m ($6^1/_2$ ft) in length. From the point at which it leaves the vaporization chamber near the top, the tube is wound downward around the vaporization chamber and then upward in the helical space between the downward windings. It is then sealed through the wall of the outside heating jacket. The mouth of the vaporization chamber is also sealed through the outer jacket and flanged for fitting with a stopper. A mouth for condenser connection is also sealed into the outer jacket.



Victor Meyer apparatus showing coiled exit tube from vaporization chamber. Breaking device with perforated discs is shown.

To minimize convection currents, the vaporization chamber is divided into several compartments by means of perforated metal discs. These are mounted on a central shaft which may conveniently function also as part of the breaking device. The perforations in the discs are for the purpose of diminishing the turbulence of flow through the annular spaces between the wall of the chamber and the rims of the discs. Such discs, but without perforations, were first used by the author more

Presented before the Division of Chemical Education at the Southeastern Regional Meeting of the American Chemical Society. Gainesville, Florida, December, 1958.

[1] WEISER, H. B., *J. Phys. Chem.*, **20**, 532 (1916).
[2] HICKS-BRUUN, M. M., *U. S. Bur. Standards J. Research*, **5**, 575 (1930).
[3] MACINNES, D. A., AND KREILING, R. G., *J. Am. Chem. Soc.*, **39**, 2350 (1917).

than twenty-five years ago. They are recommended in certain laboratory manuals.[4]

The breaking device is an adaptation of the MacInnes and Kreiling device which is here extended almost to the bottom of the vaporization chamber and on which the sample bulb is merely suspended and free to fall when crushed because it is desired to vaporize the liquid at the bottom of the chamber.

The advantage of the present design are: (1) compactness—the overall length is only about 33 cm; (2) almost complete freedom from the danger of vapor condensation; (3) durability—the apparatus is constructed of Pyrex and the helical delivery tube is free to expand and contract without developing serious strain; (4) convenience of the mouth for condenser connection—this is especially desirable when boiling liquids other than water are used.

Typical student results are given in the table. Routine vapor density determinations by students using the design of apparatus described have been less subjected to erratic errors than with the ordinary form of the apparatus.

Illustrative Student Data Using Ethylaniline (B.P. 204°C) as Boiling Liquid

Substance	$M = gRT/PV$
Benzene (78.11)	77.0, 78.2, 78.4
Chloroform (119.39)	120.0, 119.0, 120.0
Water (18.02)	17.6, 17.3, 17.4
Toluene (92.14)	93.2, 91.5
Acetone (58.08)	57.9, 57.5
Diethyl ether (74.12)	74.2, 73.7

[4] Daniels, F., Mathews, J. H., Williams, J. W., Bender, P., and Alberty, R. A., "Experimental Physical Chemistry," 5th ed., McGraw-Hill Book Co., Inc., New York, 1956, p. 10.

Division of CHEMICAL EDUCATION

American Chemical Society

At the Atlantic City September meeting of the Executive Committee, William F. Kieffer, Editor of the Journal of Chemical Education, reported that the Journal circulation was about 11,000. The "Tested Demonstrations" have sold 3,000 copies, and the "Selected Readings" over 2,000 copies.

Samual P. Massie, Chairman of the Committee on Visiting Scientists, reported that in the 1958–59 program, the total budget of the National Science Foundation-supported program was $27,000. The program was expanded to include junior colleges, high schools, and the new state of Alaska. Eleven colleges were revisited. For 1959–60 an increased budget of $55,000 is to be used for 160 three-day college visits, and 140 one-day high school visits. The Visiting Scientist Staff has been increased to 70. An advanced grant of $30,000 has been made for the 1960–61 program and an application for $25,000 for a foreign visitors program is being planned.

The activities of the Examinations Committee have again expanded. Chairman Theodore A. Ashford reported that the sales of examinations increased from $21,000 to $31,000. The sale of test booklets was 85,000, and it is estimated that over 225,000 students were tested. The increase was primarily attributed to the wider use of high school tests with the sales rising from 31,000 to 48,000 tests. Two new tests were published this year, the High School form 1959, under the chairmanship of Walter E. Hauswald, Sycamore (Illinois) High School, and Biochemistry Form 1959, under the chairmanship of Dr. Harold G. Oddy. The new chairman of the *High School Subcommittee (I)* is R. W. Woline of Oak Park and River Forest High School (Illinois). This committee has started work on a new test slated for release in the spring of 1961. Mr. Kermit Waln (Denver) has been appointed acting chairman of the *High School Subcommittee (II)* while Dr. Wilkinson is in Europe.

Seven subcommittees are actively working on new tests. The *General Chemistry* Subcommittee under the chairmanship of Dr. Wright administered two experimental forms last spring, and the new test should be ready by the spring of 1960. The *Qual-in-General* Subcommittee, under the chairmanship of Nelson Hovey, has undertaken the preparation of a Qualitative Analysis supplement to be used in general courses which devote the second semester to qualitative analysis. The parent *Qualitative Analysis* Subcommittee, under the chairmanship of Dr. Lloyd Malm, has administered two experimental forms of a test which should be published in the spring of 1960. The *Organic Chemistry* Subcommittee under the chairmanship of Dr. Nelson is working on a new one-year Organic test. The *Inorganic* Subcommittee, under the chairmanship of Dr. S. Y. Tyree, Jr., has completed two experimental forms which are to be administered in the spring of 1960. The *Graduate Level* Subcommittee with Dr. Harry G. Day as chairman held its first meeting during the fall 1959 ACS meeting. Two tests are now available in Spanish. Dr. Leo B. Lathroum of the University of Puerto Rico compiled a test from several of the General Chemistry forms, and Dr. Vincent Wottle, Catholic University of Puerto Rico, has translated Part I of the High School Form 1959.

The Executive Committeee of the Division elected or appointed the following:

Alternate Councilor: L. E. Strong, Earlham College
Member Board of Publication: J. F. Bunnett, Brown University
Representative to the AAAS Cooperative Committee on Science Teaching: H. F. Lewis, Inst. of Paper Chem.
Chairman of Committee on Institutes and Conferences: W. T. Lippincott, University of Florida

A motion was passed to create a new subcommittee of the Committeee on Teaching to be named the Subcommittee on *Experimental Curricula*. The object of this committee is to collect information on the various efforts being made to present chemistry in a new light, and to aid in the organization and development of these programs. It was agreed that the committee in its original membership should contain a representative number of participants from the 1959 Reed Conference. Chairman Smith appointed Arnold Bereit, James DeRose, H. A. Neidig, L. E. Strong, and Frank Verhoek as members of the committee.

L. E. Strong reported that the Reed Conference group had started writing textual materials for a high school course based on the chemical bond. The first section of the material has been published and was used by high school teachers in nine schools in the fall of 1959. The Reed Conference group also requested that the Division accept the copyright of all textual materials produced. However, no action was taken pending consultation with the Society's legal counsel regarding the legality and advisability of this move.

Chairman Smith reported that Dr. Mellon is investigating the nature and extent of courses in chemical literature in colleges and universities. His committee will consist of three members each from this Division and the Division of Chemical Literature.

Much of this report has been taken from the reports of the various committee chairmen, and from the Secretary's minutes. For the next three years the Division Reports will be written by Dr. Richard Ramette of Carleton College, the new elected Member-at-Large of the Division.

Edwin M. Larsen

Movies on Chemical Subjects

A year ago the Board of Directors of the American Chemical Society set up a Subcommittee on Educational Films "to establish criteria for production of educational films in chemistry, to encourage production of more such films, and to review and evaluate films in a manner similar to the present review of books." Professor A. B. Garrett of Ohio State is Chairman of this Subcommittee of the Committee on Education and Students.[1]

One of the first tasks assigned by the Subcommittee was to find out what films had recently been produced and what films were under consideration for imminent production. Some 200 colleges were solicited for information, industrial groups were contacted, and a notice of the survey was carried in *Chemical and Engineering News*. This article is a summary of the results of the survey. It is incomplete both because of incomplete coverage and because so much is occurring in this field, but does allow some conclusions which may be helpful to those using and producing films on chemical subjects.

The Survey

Four responses were requested: (1) Names and suppliers of films recently produced or strongly endorsed by the respondee, (2) names of films planned for production, (3) names of persons especially interested in educational films and their use, and (4) general comments on educational films. About 200 responses were received, of which slightly over half had information concerning the actual use of films. About a third of the colleges responding indicated no interest in educational films in chemistry.

Films Endorsed or Recently Produced

Some fifty films were specifically endorsed. About a dozen of these were produced by industries to present the chemical facts about their operations. Another dozen dealt with particular subjects like catalysis or the halogens, while half a dozen were essentially filmed lectures by outstanding chemists. The largest group of films concerned themselves with the operation of an instrument or a technique, e.g., weighing, the spectrograph, or analytical operations.

The very small number of industrial films recommended is an interesting commentary on the available films. At least several hundred are available, but only a dozen were even mentioned as useful. We should point out here that this is not the situation in the high schools, where a very large number of industrial films are used with some enthusiasm year after year. It would be interesting and worthwhile to investigate the reasons for this distinction in the use of the films. But the fact does emphasize that any study of films on chemical subjects should clearly define its potential audience, e.g., whether it is to be high school or college.

A further problem was brought to light by the number of films now extant dealing with the use of the analytical balance. Three have been available for some years, but three new ones appeared on the lists, planned or produced within the last few years. Numerous other overlapping interests in planned films were also discovered. These facts raise the question as to whether it might not be well, as a minimum, to have a mechanism for putting groups interested in similar films in contact and, perhaps, of helping them to cooperate in producing a single film better than any one group could accomplish alone. Six films on the use of analytical balances hardly seem necessary or desirable.

The increase in the number of films which discuss modern equipment and new techniques is an exciting development which can still bear much expansion. The Committee plans to publish reviews of films on spectroscopy, electron diffraction, X-ray diffraction, analytical techniques, crystal growth, and many others, and so apprise teachers of chemistry concerning these newly available methods of expanding instruction.

The tendency to have outstanding chemists filmed as they discuss their specialties is another noteworthy feature of modern productions. Many teachers feel that a major error has been made in not starting projects like this earlier. The use of such films in presenting ideas and in letting a very large group of students see a number of first class scholars in action deserves investigation. As one comment put it, "Future generations are the poorer for not having a record of men like G. N. Lewis in operation, twitching his impressive eyebrows, and throwing off intellectual sparks."

Films Planned for Imminent Production

An impressive array of groups are starting or about to start ambitious film projects. Some by now are well along into production or even finished. One set of films, with John Baxter as principal lecturer, encompasses a full high school course in chemistry in about 150 films. Shorter series have been prepared for local consumption and should be reviewed for a wider possible audience. Many were designed for TV series and have been kinescoped for other uses. It should be worth looking at these to see how many of them can be adapted to the more well-defined requirements of the classroom.

The various branches of the U. S. Government have produced a large number of films, with the Army and the Atomic Energy Commission leading the parade in numbers of films for instructional purposes.

At least two universities, Akron and Purdue, are producing series of films aimed to supplement or replace laboratory work, and many other universities are actively seeking funds to support their own projects for film production. Twenty-two different colleges listed at least one film as being planned for production.

Degree of Interest in Film Use

A large number of teachers are interested in the use of films even though they have no plans to produce any themselves. Though only twenty-two schools plan productions, about two hundred teachers from one hundred schools expressed special interest in educational films and their use. The problem of reviewing the films ought to be well within the realm of solution with this degree of interest.

Three other groups with interests similar to those of the Committee were uncovered during the survey. The Delaware Valley Local Sections in cooperation with the ACS News Service is already well into a review of some five hundred industrial films, evaluating them for use in high school courses. The American Institute of Chemical Engineers has been performing this service for engineering colleges for seven years, and the National Academy of Sciences is considering setting up a film review group.

The Place of Science Films in the Future Academic Program

It is the conviction of the Committee that the good science films of the future will occupy a place comparable to the textbook as an important tool for the teacher to use in his teaching. We do not intend or expect that they will replace the teacher. But we do feel that the art of film production has now developed to the place that it should be made use of as an important adjunct in an effective teaching program. See Figure 1.

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[1] The subcommittee solicits further information, ideas, and volunteers for reviewing. Please contact Professor A. B. Garrett, Department of Chemistry, The Ohio State University, Columbus, Ohio. The members of the committee are:

A. B. Garrett, *Chairman*, Lawrence Bromberick, J. A. Campbell, Miss Christine Jansing, William F. Kieffer, Calvin VanderWerf, Joel H. Hildebrand, Elbert C. Weaver, Edward Fuller, John F. Baxter, Edward Haenisch, and Roy L. Whistler.

Deteriorating Versus Improving Situation of Film Production

From our viewpoint it appears that the situation now gives promise of having available excellent science films for classroom use. The two new films "Vibration of Molecules" and "An Introduction to Reaction Kinetics" are pace-setters of the high quality that we must have. Other examples are the physics films made by Prof. Zacharias of the Physical Science Studies Group at MIT.

From another viewpoint the situation seems to be deteriorating with the threat of flooding the market with a large collection of inferior or mediocre "educational" films. This is the result of too many unqualified persons and companies trying to make films without the benefit of the proper know-how or critical analysis of their product. This must be minimized. We must turn to a careful program of critical film reviews for those films already produced as well as try to draw up a careful guide to film production for films being or to be produced.

A Clearing House of Science Film Information

To bring order out of chaos within a reasonable time and to make film use most effective for science teaching within the not-too-distant future, it may be desirable to establish a clearing house for Chemistry Film Production.

This could give a continuing service of film analysis and evaluation, a listing of topics recommended for film adaptations, and a guide to the production of new films.

Criteria for Successful Films

The great upsurge of interest in films and TV as teaching media has brought forth many projects for the preparation of such material. This Committee has therefore considered it desirable to outline some of the factors that should be considered in connection with such projects.

To prepare a worthy, useful film is a major undertaking. An animated film is no job for an amateur with a new camera, and a filmed lecture should be to a desk lecture as a stage play is to a dramatic reading. We list here some of the requirements:

1. Close cooperation with a highly competent, experienced production staff, a highly competent scientist in continual contact with the studio, and an excellent group of outside advisors, all interested in producing something of high quality, both scientifically and artistically.
2. Thorough command of the scientific facts, concepts, and theories involved. Without scientific accuracy the film will not gain real acceptance and will actually be detrimental to those who do use it.
3. Clear purpose in relation to a particular audience, and to the regular teacher.
4. Recognition of the demands, possibilities, and limitations of the medium.
5. Experience and demonstrated skill in scientific exposition, with a sense of high grade showmanship.
6. Facility in the use of clear, concise, precise English.
7. Cost. A recent series of recorded broadcasts cost approximately $1600 merely to record each half-hour lecture. The preparations of two 13-minute animated cartoons on Activated Complexes and Molecular Vibrations were supported by a grant of $110,000 by the Sloan Foundation; their distribution and testing by a grant of $35,000 by the Ford Foundation.

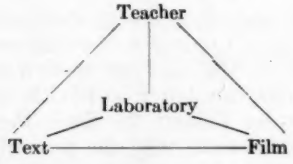


Figure 1.

The Future of the Committee

Contemplation of the poor quality of films available in the past and the high degree of current interest indicates ample room for usefulness on the part of the Committee. It actively solicits suggestions but, in the meantime, plans to proceed in the following ways:

1. Set up a clearing house for information on films in production or being considered for future production, available to all interested in producing films.
2. Collect criteria for successful films and make them available to interested producers.
3. Set up a system whereby films can be reviewed and the reviews published in the professional journals.
4. Investigate current and planned films and areas of interest and make available to possible producers information concerning subjects of interest not as yet covered.
5. Set up a clearing house on advisory matters whereby producers with scientific and technical problems can be put in touch with others with past experience in handling such problems.
6. Investigate the needs of different groups, e. g., high schools, colleges, and the general public.

Sources of Films Now Available

The Committee has not as yet had an opportunity to review any of the currently available films, but the following sources may be of interest to those especially eager to receive some of the more recent information.

"A Directory of 3660 16-mm Film Libraries," $1.00, 236 pages, Catalog No. FS 5.3:959/4, available from the Superintendent of Documents, Washington 25, D. C. The libraries then can be contacted for film catalogues.

"Catalog of Current Films—Chemistry and the Chemical Industry, April 1959," available from the Manufacturing Chemists Assn., 1825 Connecticut Ave., N. W., Washington 9, D. C.

"Integral Catalog of Scientific Films, Edition 1958," Institut für den Wissenschaftenlichen Film, Göttingen, Germany.

Public Information Service, AEC, Washington 25, D. C., will send information on their films.

High School teachers interested in the Delaware Valley Project of reviewing films on chemistry might write Miss Ann L. Farren, Research and Information Center, ACS News Service, 2 Park Ave., New York 16, N. Y.

The following recent films have been recommended to the Committee. The Committee would be most interested in comments of viewers for use in its reviews.

FILM	SUPPLIER
"Path of Carbon," Melvin Calvin	Handel Films 6926 Melrose Avenue Hollywood 38, California
"The Ultimate Structure"	North American Phillips 100 E. 42nd Street New York 17, N. Y.
"Crystal Growth"	Bell Telephone Laboratories 463 West Street New York 14, N. Y.
"Valence and Molecular Structure," Pauling (three films)	Byron, Inc. 1226 Wisconsin Avenue, N. W. Washington, D. C.
"Techniques of Organic Chemistry," Fieser	Young America Films 18 E. 41st Street, New York 17, N. Y.
"The Chemical Elements," Seaborg	NET, Indiana University
Eleven films on laboratory techniques	Audio-Visual Center Purdue University
Numerous films on freshman laboratory	Department of Chemistry University of Akron
Three films on analytical techniques, including IR Spectroscopy	Department of Chemistry Rensselaer Polytechnic Institute
"Molecular Vibrations" and "The Activated Complex"	Sutherland Productions 201 N. Occidental Avenue Los Angeles 26, California
"Principles of Chromatography"	Dept. F, H. Reeve Angel & Co. 52 Duane Street New York 7, N. Y.

Proceedings of the

Pacific Southwest Association of Chemistry Teachers

George B. Kauffman
and **Jerome S. Blank**
Fresno State College
Fresno 26, California

Separating Nd from Pr

A laboratory experiment in ion exchange chromatography

The lanthanides (elements of atomic numbers 57 to 71) provide many opportunities for illustrating the correlation between fundamentals of atomic structure and observed properties. For this reason, they are particularly suitable for today's general chemistry course with its increasing emphasis on theory. This group of elements furnishes an unparalleled example of the gradual filling of an internal electronic level while the outermost shell remains unchanged. The regular decrease in size of the tripositive lanthanide ions with increasing atomic number (the lanthanide contraction) can be correlated with their basicities, complexing tendencies, and other chemical properties (*1*). The present experiment is designed to acquaint undergraduates with the lanthanides by means of an ion exchange separation of two of their more inexpensive and contrastingly colored members using the recently developed chelating agent, ethylenediaminetetraacetic acid (EDTA) (*2*).

For a number of years, didymium was considered to be an element until, in 1885, it was finally separated into praseodymium and neodymium by Baron Auer von Welsbach (*3*, *4*, *5*). Considering the difficulties involved, the time required for the separation given here (7–8 hr) does not seem at all excessive to the authors.

A literature search reveals that the only demonstration of a separation of one lanthanide from another is that of Ce^{144} from Pr^{144} (*6*), which employs the method of valence change—a method applicable to those lanthanides possessing other oxidation numbers in addition to the common tripositive state. The method described here is in principle applicable to all the lanthanides.

The Experiment

Although unidentate ligands generally do not form complexes with lanthanides, chelating agents form strong lanthanide complexes, which increase in stability with decreasing ionic radius, i.e., increasing atomic number. The experiment presented in this paper, based on the work of Spedding, Powell, and Wheelwright (*7*), uses as eluent a 1% solution of the highly efficient complexing agent EDTA, buffered to *p*H 8.5 with ammonia. The band of lanthanides adsorbed on a column of Dowex 50W is eluted through a second column of this resin in the copper(II) form. Since the copper(II)-EDTA complex is more stable than the EDTA complexes of either neodymium or praseodymium as shown by the following equilibrium constants in which Y represents the tetravalent ethylenediaminetetraacetate anion (*8*, *9*):

$$Pr^{+3} + HY^{-3} \leftrightarrows H^+ + [PrY]^- \qquad \log K_{293} = 16.55 \quad (1)$$

$$Nd^{+3} + HY^{-3} \leftrightarrows H^+ + [NdY]^- \qquad \log K_{293} = 16.75 \quad (2)$$

$$Cu^{+2} + H_2Y^{-2} \leftrightarrows 2H^+ + [CuY]^{-2} \qquad \log K_{293} = 18.38 \quad (3)$$

the second column acts as a barrier through which the lanthanide-EDTA complexes cannot pass without decomposition, thus enhancing the separation.

The reactions occurring in Column 1 during the elution cycle may be represented by the following equilibria, assuming $(NH_4)_3HY$ as the principal eluting species:

$$\underline{NdR_3} + 3NH_4^+ \leftrightarrows \underline{3NH_4R} + Nd^{+3} \quad (4)$$

$$\underline{PrR_3} + 3NH_4^+ \leftrightarrows \underline{3NH_4R} + Pr^{+3} \quad (5)$$

$$Nd^{+3} + HY^{-3} \leftrightarrows H^+ + [NdY]^- \quad (6)$$

$$Pr^{+3} + HY^{-3} \leftrightarrows H^+ + [PrY]^- \quad (7)$$

in which R represents one equivalent of resin anion. Adding (4) and (6) gives:

$$\underline{NdR_3} + 3NH_4^+ + HY^{-3} \leftrightarrows \underline{3NH_4R} + H^+ + [NdY]^- \quad (8)$$

while adding (5) and (7) gives:

$$\underline{PrR_3} + 3NH_4^+ + HY^{-3} \leftrightarrows \underline{3NH_4R} + H^+ + [PrY]^- \quad (9)$$

Equations (8) and (9) represent the over-all net reactions occurring in Column 1, the displacement of the lanthanides from the resin by ammonium ion. The lanthanides, now in solution as EDTA complexes, become influent for Column 2. Since the neodymium complex is more stable than the praseodymium complex (*cf.* equations (1) and (2)), reaction (8) proceeds to the right to a greater extent than reaction (9), and consequently, at first, the concentration of neodymium in this solution is greater than that of praseodymium, while later the exact reverse is true.

The reactions occurring in Column 2 during the elution cycle may be represented by the following equilibria:

$$3\underline{CuR_2} + 2[NdY]^- + HY^{-3} \leftrightarrows 2\underline{NdR_3} + H^+ + 3[CuY]^{-2} \quad (10)$$

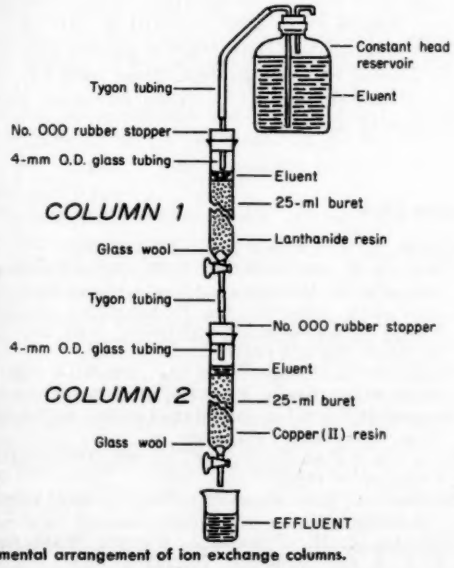
$$3\underline{CuR_2} + 2[PrY]^- + HY^{-3} \leftrightarrows 2\underline{PrR_3} + H^+ + 3[CuY]^{-2} \quad (11)$$

Reactions (10) and (11) proceed to the right to a large extent since Cu^{+2} forms a more stable complex with EDTA than either Nd^{+3} or Pr^{+3} (*cf.* equations (1), (2), and (3)) and also since Nd^{+3} and Pr^{+3} have greater affinities for the resin than does Cu^{+2}, trivalent ions being more strongly adsorbed than divalent ions (*11*). Since the neodymium complex is more stable than that of praseodymium, reaction (11) goes to the right to a larger extent than reaction (10), and the praseodymium is redeposited on the resin to a greater extent than is the neodymium. After all the copper has been eluted from Column 2 as $H_2[CuY]$, the lanthanides as $H[NdY]$ and $H[PrY]$ are eluted according to equations (8) and (9).[1] Since, as previously pointed out, reaction (8) goes to a larger extent than reaction (*9*), a further enrichment of the earlier fractions with respect to neodymium again occurs. Doubling equation (8) and adding to equation (10) or doubling equation (9) and adding to equation (11) gives, after division of the result by three:

$$2NH_4^+ + HY^{-3} + \underline{CuR_2} \leftrightarrows \underline{2NH_4R} + H^+ + [CuY]^{-2} \quad (12)$$

showing that the over-all net reaction occurring in Column 2 consists of the displacement of copper from the resin by ammonium ion and elution of this copper as $H_2[CuY]$.

The reactions involved are all reversible. Throughout the elution cycle, the steady replacement of NH_4^+ and HY^{-3} ions by incoming eluent and removal of reaction products by drainage of effluent shift all the equilibria to the right in accordance with Le Chatelier's rule.



Experimental arrangement of ion exchange columns.

[1] Since $H_2[CuY]$, $H[NdY]$, and $H[PrY]$ are all moderately strong acids (*10*), the effluent containing these substances is acidic (*p*H *ca.* 2). If the *p*H of the eluent is too low, the flow may be obstructed by precipitation on the columns of these substances or EDTA.

Materials

Cation Exchange Resin. Dowex 50W-X8 (light yellow), H^+ form, 50–100 mesh. Dowex 50 (dark brown) may be used, but elution bands and color changes will not be visible.

Lanthanide Stock Solution. 60 ml of 6 *M* HCl is cautiously added (*Hood!*) to an approximately equimolar Nd-Pr mixture consisting of 8 g of Lindsay Chemical Company Code No. 623 "neodymium" oxide (85% Nd_2O_3, 11% Pr_6O_{11}) and 6 g of Lindsay Chemical Company Code No. 726 praseodymium oxide (99% Pr_6O_{11}):

$$\underline{Nd_2O_3} + 6H^+ \rightarrow 2Nd^{+3} + 3H_2O \quad (13)$$

$$\underline{Pr_6O_{11}} + 22H^+ + 4Cl^- \rightarrow 6Pr^{+3} + 11H_2O + \overline{2Cl_2} \quad (14)$$

After most of the effervescence has subsided, the resulting yellow-green dichroic solution is heated to dryness (*Hood!*) to remove excess acid in order to prevent reversal of equilibria (15) and (16). The whitish green residue is taken up in *ca.* 100 ml of distilled water, and HCl is added dropwise (*ca.* 1 ml) until the milky green suspension just becomes a clear yellow-green dichroic solution. When diluted to 200 ml, this furnishes enough solution for five runs.

1 M Copper(II) Sulfate. 62.5 g of $CuSO_4 \cdot 5H_2O$ plus 2 ml of H_2SO_4 dissolved in distilled water and diluted to 250 ml (enough for seven runs).

Eluent. 40 g of EDTA (practical grade is satisfactory if colored impurities are absent) is placed in a 4-liter beaker with *ca.* 3 liters of distilled water, and concentrated aqueous ammonia is added (*ca.* 38 ml) until the white powder has dissolved and the *p*H of the resulting solution is 8.5 (Hydrion paper). The solution is diluted to 4 liters (enough for six runs).

0.1 M Ammonium Oxalate or Oxalic Acid. 7.1 g of $(NH_4)_2C_2O_4 \cdot H_2O$ or 6.3 g of $H_2C_2O_4 \cdot 2H_2O$ is dissolved in distilled water and diluted to 500 ml.

Procedure

Adsorption Cycle. Aqueous slurries prepared from 8-g and 12-g samples of Dowex 50W-X8 are poured into two separate 25-ml burets provided with retaining plugs of glass wool. As the excess water drains, the resin settles forming light yellow beds. Care must be taken at all times not to allow the liquid levels to fall below the top of the resin beds.

With the stopcock open, 40 ml of lanthanide stock solution is poured onto the shorter column (Column 1), converting it to the grayish tan lanthanide form:

$$Nd^{+3} + 3\underline{HR} \rightarrow \underline{NdR_3} + 3H^+ \quad (15)$$

$$Pr^{+3} + 3\underline{HR} \rightarrow \underline{PrR_3} + 3H^+ \quad (16)$$

Similarly, 35 ml of copper(II) sulfate solution is poured onto the longer column (Column 2), converting it to the bluish green copper(II) form:

$$Cu^{+2} + \underline{2HR} \rightarrow \underline{CuR_2} + 2H^+ \quad (17)$$

Both columns are then rinsed until the *p*H of the effluents rises to that of distilled water, an indication that all unadsorbed ions have been removed. The shrinkage of the resin on conversion from the water-equilibrated hydrogen form to the water-equilibrated lanthanide (*ca.* 13%) and copper(II) forms (*ca.* 8%) is in accord with the general rule that the affinity of a given cation for a cation exchange resin usually increases with increasing charge as does the shrinkage on conversion to a given ionic form (*11*).

Elution Cycle. The columns are connected in vertical series as shown in the accompanying figure. The liquid level in Column 2 is kept as low as possible (*ca.* 1 ml above the top of the resin bed) in order to minimize mixing of neodymium and praseodymium. The stop-

cock on Column 1 is opened completely, and the stopcock on Column 2 is adjusted to a flow rate of *ca.* 1.4–1.5 ml/min (2.4–2.6 cm/min). The effluent is collected in a 600-ml beaker.

Displacement of the lanthanides from Column 1 by ammonium ion is evidenced by a change in resin color from grayish-tan to light yellow. Simultaneously, the lanthanides are redeposited on Column 2 where they appear as a yellowish-green band (fluorescent green under ultraviolet light[2]) displacing the darker bluish-green copper band at a rate of *ca.* 6–7 cm/hr. Copper appears in the effluent as the deep blue EDTA complex.

After about 3 hr (times and volumes vary with flow rate and resin packing), the lanthanides have been completely displaced from Column 1, and the leading edge of the lanthanide band, now on Column 2, has assumed a reddish tinge. Soon four bands are visible on Column 2—the bluish-green copper band at the bottom, the reddish neodymium band, the yellowish-green praseodymium band, and finally the light yellow ammonium band at the top.

When the copper has been completely eluted (350–375 ml of effluent; *ca.* $4^1/_2$ hr), collection of the lanthanide fractions is begun, using 150-ml beakers. The approximate volumes and times required for these fractions are: the bluish-violet neodymium fraction, 75 ml, $5^1/_2$ hr; the pale greenish-violet intermediate fraction, 90 ml, $6^3/_4$ hr; and the green praseodymium fraction, 125 ml, $7^1/_2$ hr. After all the neodymium has been eluted, the flow rate may be increased to elute the praseodymium more quickly. With the complete removal of praseodymium, the *p*H of the effluent rises from about 2 to about 8. After the columns are disconnected and rinsed with distilled water, they are ready for another run.

In order to show the true colors of neodymium and praseodymium ions, each of the three lanthanide-containing fractions is acidified with 5 ml of HCl and electrolyzed[3] at *ca.* 0.5 ampere for 5–10 min to remove contaminating copper(II) ion. The previously obscured pink neodymium color is now visible in the first fraction, while the intermediate fraction appears almost colorless. The third fraction appears unchanged since the small amount of copper originally present had virtually no effect on the green color of the praseodymium. However, the student should electrolyze this fraction to convince himself that the color is not due to traces of copper. The pink and green colors of the neodymium and praseodymium fractions are pale but intense enough to be seen at a distance, especially against a white background.

Recovery of Neodymium and Praseodymium (Optional). The fractions may be analyzed spectrophotometrically (Nd at 522 mμ and Pr at 444 mμ) using 10-cm absorption cells. The lanthanides may be recovered as oxides by adding excess 0.1 *M* ammonium oxalate or oxalic acid,[4] filtering the resulting oxalate, charring the filter paper in a crucible, and igniting at 800° C for 30–40 minutes. Visual comparison of the colors of the oxalates and oxides obtained from the fractions with those of the pure materials and the original mixture can be used to show qualitatively the extent of purification. Spectrophotometric analyses of chloride solutions prepared from the oxides showed the "neodymium" and "praseodymium" fractions may contain as high as 25% of the other lanthanide. It should be emphasized that the primary purpose of this experiment is merely to illustrate visually with a reasonable expenditure of time the ion exchange separation of two adjacent lanthanides. If *pure* neodymium and praseodymium are desired, the more time-consuming procedure recommended by Spedding, Powell, and Wheelwright (7) should be followed.

The experimental conditions given above were chosen on the basis of exploratory studies of a number of variables and represent a compromise between time requirements and purity requirements. These variables (sample size and composition, EDTA concentration, *p*H of eluent, flow rate, resin crosslinkage, and relative lengths of columns) may be investigated in the school laboratory as to their effect on the separation. Since the flow can be interrupted at any time during the experiment, the separation can be performed in the course of several laboratory periods. For the same reason, it can also be used as a serialized lecture demonstration, the lecturer exhibiting the columns at various stages of the separation.

[2] "Mineralight" Model SL (without filter), Ultra-Violet Products, Inc., 145 Pasadena Ave., South Pasadena, Calif.

[3] Sargent-Slomin electrolytic analyzer, Catalogue No. S-29464, E. H. Sargent and Co., Chicago, Ill.

[4] Addition of oxalate and swirling of the suspensions is especially recommended for making the colors visible at great distances.

Acknowledgment

The authors gratefully acknowledge the assistance of the Dow Chemical Company, which provided samples of both resin and EDTA, and of the Lindsay Chemical Division, American Potash and Chemical Corporation, which provided lanthanide samples. For valuable advice, our thanks go to Drs. Howard E. Kremers and M. M. Woyski of the last-named company and to Dr. Jack E. Powell of Iowa State College and Dr. R. C. Vickery of the Research Chemicals Division, Nuclear Corporation of America.

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Chemical Aspects of Open-Heart Surgery

Cardiac surgery has advanced so rapidly that certain types of corrective surgical procedures now possible were either in early experimental stages or unheard of 5 to 10 years ago. One of the more amazing advances has been the development of open-heart surgery in which a surgeon carries out repairs within the various chambers of the heart while the surgical field is in full view. Many problems had to be solved before the present level of success was attainable. In order to open the heart, it was necessary to temporarily halt the circulation of the blood with its important supply of oxygen. The highest centers of the central nervous system, due to their relatively high metabolic rate, are particularly susceptible to damage from lack of oxygen. These centers, however, can be deprived of oxygen for periods up to 5 min without damage, allowing less complicated surgery to take place while the circulation is temporarily interrupted for this period of time. In order to extend the period in which more complicated repairs could be attempted, the technique of hypothermia or low temperature surgery was developed. By cooling the patient to temperatures below normal, the metabolic rate of the tissues is lowered and thus there is a decreased requirement for oxygen. This technique lengthened surgical periods to 10 min.

This was still insufficient for carrying out the more extensive repairs required for some of the more complicated abnormalities encountered. If it were possible to bypass the heart and lungs while maintaining circulation and a near normal physiology in the rest of the body, surgery could be performed for a longer period of time. This idea sparked the development of various types of "heart-lung" pumps, which are man's attempt to substitute mechanically for some of the functions of the living heart and lungs. In operation, the various tubes and reservoirs are first primed with blood of the patient's type. Connections are then made to the superior and inferior vena cavae with plastic tubing, leading the blood into reservoirs of the pump instead of the right atrium of the heart. The blood passes through the oxygenator, taking on oxygen and giving up carbon dioxide, and then flows through a pumping device from where it is directed into one of the large arteries of the body by means of plastic tubing. Thus the circuit is completed. The heart still receives its own supply of blood to maintain the integrity of the myocardium. The chambers having been bypassed can now be opened and repairs made. The outflow of blood from the coronary system is withdrawn by a vacuum pump, thus keeping the surgical field free of blood. This technique permits surgery on the heart for periods up to an hour. Although this type of extremely delicate and complicated surgery has been mastered by thoracic surgeons, it would not be successful if the chemistry of the blood and body were disregarded.

Although the chemistry involved here might appear to be comparatively simple at first glance, we must not lose sight of the fact that we can seldom confine a change or reaction to a specific biochemical system. The living body is composed of wonderfully coordinated biochemical systems and when we attempt to alter the normal activity of a particular system in a particular organ, we must be aware of possible changes occurring in other organs with similar systems. No one organ can truly be separated from another when we are concerned with physiological and biochemical function, unless we take special measures to isolate a patricular organ or tissue.

Within the body, the concentration of the various constituents of the blood and tissues are automatically controlled within relatively narrow limits. When the blood leaves the body to flow through the tubes and chambers of the heart-lung pump for extracorporeal circulation and is subjected to the various stresses encountered in the mechanical system, certain changes can occur which are not easily controlled by normal processes.

Acid-Base Balance

The acid-base balance of the body which is necessary for maintenance of proper *p*H of the fluids and tissues depends largely on the amount of carbon dioxide in the blood. When an excess of this substance is retained, there is an increase of carbonic acid, a drop in *p*H, and a resultant acidosis; on the other hand, removal of too much CO_2 will result in an alkalosis because of a decrease in hydrogen ion concentrations. With our par-

Presented at the 21st Summer Conference of the New England Association of Chemistry Teachers, University of Connecticut, Storrs, August, 1959.

ticular type of oxygenator, we found that carbon dioxide "washout," with a rise in *p*H, occurred when pure oxygen was fed into the oxygenator. Series of experiments were conducted in which the oxygen was combined with various percentages of CO_2 while the *p*H was monitored at 5 min intervals throughout the perfusion. Our results indicated that 1–2% CO_2 98–99% O_2 combination maintained the *p*H within the normal physiological range with a minimum variability.

Temperature and Gas Solubility

Another factor is that of the effect of temperature on the solubility of gases in the blood. It is necessary to maintain the temperature of the blood within the extracorporeal circulation at the same level as, or perhaps 1 or 2 degrees higher than, that of the patient. Should the temperature of the blood leaving the oxygenator be lower than that of the patient there would be a tendency for oxygen to leave the blood in the form of bubbles. Along with the solubility factor, the mechanical agitation involved in the oxygenation of blood may create many bubbles which can be carried into the arterial system. These bubbles from both sources could very well produce gaseous embolism with resultant tissue damage and even death. In order to avoid these difficulties close temperature control of the oxygenator, prevention of overagitation of the blood, and removal of bubbles are necessary.

Coagulation Control

Another difficulty that may arise is that which involves the coagulating mechanism of the blood. To prevent clotting within the systems, a given quantity of heparin, an anticoagulant, is injected into the patient and into the blood priming the apparatus. This is then neutralized at the end of the perfusion by adding a substance such as protamine to the system. However, when the blood is exposed to the inner surfaces of the man-made appartus for long periods of time and is subjected to continuous agitation, clot formation may be initiated which can remove essential clotting elements from the blood such as the thrombocytes, fibrinogen, and prothrombin. When this occurs, the blood will have a decreased ability to coagulate following the perfusion, and a tendency to hemorrhage will follow.

These are probably the most important factors, although by no means all that are involved in the attempts to maintain a normal physiology with extracorporeal circulation.

Muscular Control by Ion Balance

Aside from the physiological aspects, there is a specific problem with which we are engaged at present.

When the "heart-lung" pump assumes the duties of the heart and the lungs, the heart still beats rhythmically so that the surgeon must perform his delicate work on a moving tissue. The ideal situation would be one where there is a nonmoving heart during surgery. Workers in this field have experimented with many chemicals in an attempt first to bring the heart to a standstill and then most importantly, to restore the normal beat at the conclusion of the surgery.

We are all aware of the importance of certain ions in the normal activity of living tissue. In particular, we refer to potassium, calcium, and sodium ions. Some recent work also implicates magnesium to some extent. By altering the ratios of the above ions, changes can be brought about in the activity of the heart muscle. For instance, an increase in the potassium ion concentration will cause the heart muscle to become flaccid and the rhythmical beat will cease. We can also lower the calcium ion concentration to produce the same effect. If it were possible to control the upset of the ionic ratios so that the beat was stopped during surgery and then was resumed at its conclusion, we would be able to apply this action routinely.

The literature refers to "potassium arrest" when potassium citrate is employed for this purpose. The theory is that this salt upsets the K-Ca ration by increasing the potassium concentration. We were not convinced that this chemical produced a true "potassium arrest," but that actually the citrate was binding ionized calcium, and thus the arrest was produced by a decrease in calcium. We therefore set up a schedule of experiments involving the salts potassium citrate, potassium chloride, and sodium citrate. Solutions of varying concentration of the salts were mixed with blood. The aorta was occluded with a clamp at a point above the heart thus interrupting circulation to the myocardium. The chemical-blood mixtures were injected into the aorta below the clamp so that the mixtures entered into the coronary system of the heart. The injections were made at varying rates to determine minimal quantities of the particular chemical necessary for stopping the heart. The actual quantity of the chemical stopping the heart was calculated in mg/Kg and meq/Kg of body weight. In most of our experiments we used only one chemical at a particular concentration per operation. If the action were due primarily to potassium, standstill should be produced with equivalent amounts of both the citrate and the chloride. However, if our premise were correct, the citrates of both potassium and sodium should produce standstill. Our results were as follows:

In a series of experiments the average dose of potassium chloride and potassium citrate necessary to produce arrest was 1.02 meq/Kg for the chloride and 0.81 meq/Kg for the citrate.

The dose of sodium citrate necessary for arrest was 0.38 meq/Kg.

We also tested sodium phytate and found that 0.34 meq/Kg was sufficient to produce cardiac arrest. Sodium lactate has also been used for this purpose by others.

The one action in common among these various substances appears to be their ability to combine with ionized calcium.

We can tentatively conclude that cardiac arrest is produced with smaller quantities of chemicals when the calcium ions are bound than by increasing the concentrations of the potassium ion.

It is also possible that other chemicals having this ability, such as the newer chelating agents, may be useful in this work.

Although we have succeeded, as have others, in bringing about elective cardioplegia we are still very much concerned with the fact that the recovery is not uniformly predictable for safe, routine use. We plan to continue our studies on the underlying mechanisms of cardiac function so that we may gain a better understanding of the various factors influencing cardiac activity.

Chem Ed

LETTERS

To the Editor:

Minor modifications of the method previously outlined in the JOURNAL (J. CHEM. EDUC., **36**, 81 (1959)) have enabled us to use the densitometer satisfactorily in the analysis of solutions in the ultraviolet and infrared regions. Good absorption was obtained for the following in the ultraviolet: hydrogen peroxide, benzoic acid, carbon disulfide, quinhydrone, formic, lactic, and oleic acids. In the infrared, good absorption was obtained for aniline, benzene, furfural, and carbon disulfide.

Further information will be supplied to interested correspondents.

SISTER HELENE VEN HORST
AND HELEN TANG

MARYCREST COLLEGE
DAVENPORT IOWA

To the Editor:

Does the emission of alpha, beta, and gamma rays from radioactive atoms occur simultaneously or in an "either or" pattern? That question was prompted after noting that many general chemistry textbooks contain the diagram showing all three being emitted, presumably at the same time. A further examination for the treatment of other aspects of radioactivity resulted in the following inventory:

One-third of the books implied rather than explicitly stated the source of the rays. Only two-thirds stated the composition of the nucleus. Four-fifths did *not* point out that there are no alpha or beta particles in that nucleus. Two-thirds of the books failed to explain the creation of the alpha particles from protons and neutrons nor did they propose an explanation for the nuclear source of the beta particles. Gamma rays were likewise without explanation in two-thirds of the books assessed. Only one-fifth mentioned the ultimate electrical neutrality of the residue of the disintegrated atom.

While the number of books scanned is not adequate for any convincing conclusion, there is enough evidence to alert their users to a concern for better coverage. Such an incomplete treatment of a topic so frequently before the reading public warrants more explicit information. Is it presumptuous to propose that the authors of our chemistry textbooks give special scrutiny to this topic in the next revision of their books?

B. CLIFFORD HENDRICKS

LONGVIEW, WASHINGTON

To the Editor:

May I ask that the attention of your readers be directed to the following pair of contrasting opinions about performing the very necessary operation of cleaning laboratory glassware. I offer no comment, but would be interested in hearing opinions based on the experience of others.

"Another point which might be emphasized is the complete unsuitability of the chromic acid-sulphuric acid mixture so often used for cleaning glass; it etches the surface, which cannot afterwards be washed clean. . .the use of this mixture should be banned in every laboratory." PARTINGTON, J. R., "An Advanced Treatise on Physical Chemistry," Longmans, Green and Company, New York, **1951**, Vol. II, p. 281.

"Of the various cleaning agents in common use, the Bureau prefers fuming sulfuric acid or a chromic-sulfuric acid mixture." HUGHES, J. C., "Testing of Glass Volumetric Apparatus," National Bureau of Standards Circular 602 (April 1, 1959), p. 9.

CRAYTON M. CRAWFORD

MISSISSIPPI STATE UNIVERSITY
STATE COLLEGE

To the Editor:

In the October, 1959, issue Carswell and Lawrance[1] describe the separation of protactinium-234 from thorium-234, and its use for half-life demonstrations.

We, too, use protactinium-234 for this purpose, but extract it directly from uranyl nitrate solution by the following method.

10 ml of 12% uranyl nitrate solution are acidified with 3 ml concentrated nitric acid, 6 ml of 1½% cupferron solution added, and the solution extracted with 12 ml amyl acetate. The organic layer is counted in a liquid Geiger counter of the type described by Veall[2] (a Mullard counter MX 124/01, was used in our work), and the decay of protactinium-234 may be observed.

If the aqueous layer, instead of the organic one, is counted, a growth curve for protactinium-234 may be observed.

The liquid Geiger counter used in this demonstration is, of course, insensitive to α-radiation and the low energy β-radiation from thorium-234. Once protactinium-234 has been separated from its parent, therefore, its growth or decay may readily be observed, via its energetic β-radiation, without interference from the other nuclides present.

R. W. C. BROADBANK
S. DHABANANDANA

LEICESTER COLLEGE OF TECHNOLOGY
AND COMMERCE
LEICESTER, ENGLAND

[1] CARSWELL, D. J., and LAWRANCE, J., J. CHEM. EDUC., **36**, 499 (1959).

[2] VEALL, N., *Brit. J. Radiol.*, **21**, 347–51 (1948).

Chem Ed

BOOK REVIEWS

Russian for the Scientist

John Turkevich, Professor of Chemistry and *Ludmilla B. Turkevich*, Lecturer in Russian, both of Princeton University. D. Van Nostrand Co., Inc., Princeton, New Jersey, 1959. ix + 255 pp. 16.5 × 23 cm. $5.95.

Scientific Russian

George E. Condoyannis, Saint Peter's College, Jersey City, New Jersey. John Wiley & Sons, Inc., New York, 1959. xii + 225 pp. 14 × 17 cm. Spiral bound. $3.50.

The recent publication of these two textbooks devoted to the scientific aspects of the Russian language is particularly welcome as we enter the third year of the Space Age. The manner in which Russian is taught to scientists and engineers is a matter of controversy. One group of teachers insists that a student should get a thorough training in the traditional basic elements of the Russian language, in general, before the specific scientific aspects are considered. A second group, however, maintains that the specific aspects of the scientific language, particularly if the student only wants *to read*, are unique enough to effect a considerable streamlining of the traditional Russian language course. It is of interest, therefore, that these two textbooks are representative of the two viewpoints.

The textbook written by Professor and Mrs. Turkevich definitely leans toward the first methodology. It is an excellent, traditional type of Russian language grammar with the substitution of technical terms for the usual nontechnical expressions. Thus, the exercises have questions such as "Where is the sulfur?" instead of "Where is the chair?" The book has several unique features such as an example of a letter which one can write to a Soviet scientist requesting a reprint, a list of the chemical elements, pictures and names of simple chemical apparatus, illustrative tables concerning the verbs of locomotion, and the presentation of the Cyrillic alphabetical characters in their cursive and script forms.

Both the organization of the text and the intent of the authors is that the book be used in classroom presentation with a teacher; it is not recommended for home study.

The order of the noun declensions is the traditional nominative, genitive, dative, accusative, instrumental, and prepositional (NGDAIP). Each chapter has an admirable selection of exercises. It is felt, however, that the vocabulary listings necessary to complete the exercises might better be placed before them, instead of after. The present set-up can lead to some confusion and a great deal of page-turning.

Technical readings in aeronautical engineering, biology, chemistry, and physics are provided beginning with Lesson 7, (p. 53). Although the reviewer is sympathetic with the authors' intent to expose the student to scientific text as soon as possible, he feels that a more gradual approach to technical readings would be desirable, particularly since very few parts of speech have been grammatically discussed by p. 53. Thus, the authors place an asterisk after each adjective in the text since adjectives are not explained until p. 100. A similar problem involves the verbal participles, a most frequently used verbal form in the scientific Russian literature, which are not discussed until p. 150.

The book is well bound and printed, is relatively free of spelling errors, and has both Russian-English and English-Russian glossaries and an index.

The textbook prepared by Professor Condoyannis is representative of the second method of teaching Scientific Russian. The first two lessons of the text (pp. 1–36) are devoted to the alphabet, pronunciation, and a concise general review of Russian grammatical highlights. The next five lessons (pp. 37–119) then review and expand the previous lessons by considering the details of nouns, adjectives verbs, pronouns, word order, and word-building which are necessary to allow the scientist and engineer to obtain a toe-hold in his start towards the mastery of Russian scientific literature. This portion of the book constitutes a good home-study course for the scientist. Five additional lessons (pp. 120–219), a master verb table, and a supplementary list of verbs conclude the book; this section again considers the parts of speech, but in a yet more detailed fashion with regard to irregularities, subtleties, and special treatments. It enhances the value of the book as a reference work.

Excellent features of the book are a high-frequency word list, warnings of exceptions-to-rules, irregularities, etc., complete translations of numerals when they occur in the readings, and good discussions on cognates and word-building.

Questionable features, from the reviewer's point of view, are (1) the author's rather different system (Lesson 1) to explain the pronunciation of Russian words, particularly since he states that "The resulting pronunciation may not always be understandable to a Russian, but will suffice for communication of Russian words between Americans" (p. 2); (2) the use of the different NAGPDI noun-declension order (see above), especially since there is no indication to the student that this order deviates from traditional textbooks; (3) the collection of all the explanatory footnotes to the various reading exercises at the end of each lesson instead of being placed under the appropriate text.

The book is reminiscent, in a concise fashion, of Scientific Russian by Professor James W. Perry, the pioneering attempt to teach Russian to scientists.

It is well-printed and also relatively free of spelling errors; it has no glossary or detailed index. It is regrettable that the publishers use a spiral plastic binding and paper covers since a conscientious student will have numerous occasions to refer to the text by turning its pages.

Neither of the above texts incorporates a composite listing of frequently used (1) abbreviations, (2) idiomatic expressions,

Reviewed in This Issue

John Turkevich and *Ludmilla B. Turkevich*, Russian for the Scientist
George E. Condoyannis, Scientific Russian
E. H. Rodd, Editor, Chemistry of Carbon Compounds. Volume 4B: Heterocyclic compounds
Eugene Müller, Editor, Methoden der Organischen Chemie. Volume 1, Part 2
N. N. Semenov, Some Problems in Chemical Kinetics and Reactivity. Volume 2, translated by *Michel Boudart*
N. N. Semenov, Some Problems in Chemical Kinetics and Reactivity. Volume 2, translated by *J. E. S. Bradley*
J. E. Salmon and *D. K. Hale*, Ion Exchange. A Laboratory Manual
Gmelin Institute, Editors, Gmelins Handbuch der Anorganischen Chemie. Special Volume: Aliphabetic Series to Systematic Subject Index
E. H. E. Pietsch and the Gmelin Institute, Gmelins Handbuch der Anorganischen Chemie. System 15: Silicon, Part C, Organos Silicon Compounds
E. H. E. Pietsch and the Gmelin Institute, Gmelins Handbuch der Anorganischen Chemie. System 5. Fluorine Supplement
Kekulé Symposium, Theoretical Organic Chemistry
Walter J. Hamer, Editor, The Structure of Electrolytic Solutions
A. V. Topchiev, Nitration of Hydrocarbons and Other Organic Compounds, translated by *Catherine Matthews*
Emilio Segre, *Gerhart Friedlander*, and *Walter E. Meyerhof*, Editors, Annual Review of Nuclear Science. Volume 8
R. A. Robinson and *R. H. Stokes*, Electrolytic Solutions
J. Honeyman, Editor, Recent Advances in the Chemistry of Cellulose and Starch
D. W. G. Ballentyne and *L. E. Q. Walker*. A Dictionary of Named Effects and Laws in Chemistry, Physics and Mathematics.

or (3) prepositional phrases encountered in technical literature; the latter two are scattered throughout the footnotes.

It has been the reviewer's experience in teaching Scientific Russian to research scientists of diverse disciplines that the inclusion of a short, general description of the organizational, geographical, and personnel structure of the Academy of Sciences of the U.S.S.R. is most helpful.

It leads to a description of both scientific institutions and research workers, and the nature and contents of the respective journals and articles which they publish. Neither of the above textbooks contains such material, nor are pages from the major Soviet technical journals presented as examples of the literary style used by research authors.

Most of the technical readings are taken from encyclopedias and high school texts. These are of definite value in learning to read but they should be supplemented with examples from journals (at least, *Doklady*) of a literary style somewhat different from that encountered in the above. One may reflect on a Soviet scientist, who has learned Scientific English by reading excerpts from the *Encyclopedia Britannica*, being confronted by a page of a current issue of the *Journal of the American Chemical Society*.

IRVING S. BENGELSDORF
Texas-U.S. Chemical Co.
Parsippany, New Jersey

Chemistry of Carbon Compounds. Volume 4B: Heterocyclic Compounds

Edited by *E. H. Rodd*. Elsevier Publishing Co. Sole distributors for the USA, D. Van Nostrand Co., Inc., Princeton, New Jersey, 1959. xviii + 655 pp. Tables. 16 × 23 cm. $24.

The present text constitutes the second portion of Volume 4 of Rodd's modern comprehensive treatise, continuing the systematic survey of heterocyclic compounds begun in Volume 4A. Well known and widely used by organic chemists, Volumes 1A through 3B of this series have reviewed the pertinent literature on the subject of aliphatic, alicyclic, and aromatic compounds. The present eight chapters, under the authorship of seven outstanding contributors, begin with an examination of six-membered ring compounds containing one hetero-oxygen or sulfur atom, then continue with a survey of a wide variety of synthetic and naturally occurring heterocycles including flavones, brazilins, haematoxylins, cyanins, indigoids, porphins, pyridazines, pyrimidines, and pyrazines. An interesting and informative chapter by I. G. M. Campbell and T. S. Stevens is included, surveying compounds containing such "unusual hetero atoms" as silicon, phosphorus, arsenic, antimony, bismuth, germanium, and halogen.

Volume 4B of Rodd continues to display the excellence, lucid prose and careful editorship of its predecessors. As evidence of the latter characteristic an Errata sheet is included with the present text; it contains a mere 36 new corrections, mostly typographical, to all seven previous volumes in this series. In addition to the more than 200 odd periodicals used as source material in Volume 4A, some 40 additional journals have been referred to in the present volume. The index to Volume 4B constitutes some 74 pages containing approximately 7000 entries.

Following the advent of Volume 1A of Rodd's comprehensive treatise, it became quite obvious that "Chemistry of Carbon Compounds" would become the single most useful modern compendium for the organic chemist actively engaged in research. Subsequent volumes of this series, including the present one, have fully confirmed this initial evaluation.

WILLIAM A. BONNER
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Stanford, California

Methoden der Organischen Chemie. Volume 1, Part 2

Edited by *Eugene Müller*, Tubingen. 4th ed. Georg Thieme Verlag, Stuttgart, Germany, 1959. xlv + 1017 pp. Many figs. and tables. 18 × 26 cm. $46.65.

There was the old chemist who was so narrow minded he could peep through the keyhole with both eyes open. Although it is now recognized that keeping both eyes open when staggering around the laboratory is a virtue, the more vexing problem of attempting to enlarge the interocular space may find a partial solution through the habitual reading of "Die Methoden der Organischen Chemie."

Part II of Volume I in this series is a continuation of the survey of general laboratory practice; it is divided into four general divisions.

The first section (188 pp.) on grinding dispersion, particle-size analysis, etc., not only describes the variety of equipment available, but surveys the theoretical and practical aspects as well. The material on foams and emulsions, together with the discussion on stabilizers and the breaking of these systems, is especially complete.

The second division (576 pp.) reviews a variety of general laboratory techniques: the handling of gases, explosive materials, small quantities of matter, high pressure equipment, and vacuum procedures. It concludes with a survey of heating, cooling temperature: measurement, control, and recording.

The third part (122 pp.) is a description of the properties and purification of the more important solvents used in laboratory practice, and concludes with a 13 page summary of the properties of drying agents.

The final portion of the book (56 pp.) contains safety precautions for a diversity of types of laboratory accidents and concludes with a discussion of the compounds of known carcinogenic hazards.

This volume is dedicated to Hans Meerwein on the anniversary of his eightieth birthday. It sustains the high level of thoroughness exhibited in the other volumes of this series. The literature for the most part is covered up to 1958. The index contains over 2000 entries.

GEORGE HOLMES RICHTER
The Rice Institute
Houston, Texas

Some Problems in Chemical Kinetics and Reactivity. Volume 2

N. N. Semenov, Academy of Sciences of U.S.S.R. Translated from the Russian by *Michel Boudart*. Princeton University Press, Princeton, New Jersey, 1959. 331 pp. 86 figs., 30 tables. 15.5 × 23 cm. Paper bound. $4.50.

Some Problems in Chemical Kinetics and Reactivity. Volume 2

N. N. Semenov, Academy of Sciences of U.S.S.R. Translated from the Russian by *J. E. S. Bradley*. Pergamon Press, Inc., New York, 1959. x + 168 pp. 73 figs., 21 tables. 14.5 × 22 cm. $5.

The original book was published in Russian in 1954, and was an expanded version of a paper given at the opening of a symposium. Two separate English translations are appearing, as listed above. Both translations are appearing in two volumes, and the first volumes have already been reviewed in THIS JOURNAL (**36**, 475 (1959)). The present volume by Boudart contains chapters on Competition between Chain Reactions and Reactions Between Saturated Molecules, Thermal Explosions, Chain Ignition, Chain Ignition in Hydrogen-Oxygen Mixtures, Chain Interaction, and Chain Reactions with Degenerate Branching. It also contains three appendixes: The Method of the Activated Complex, Quantum Mechanical Calculations of the Activation Energy, and Additions to Volume 1. Volume 2 of the Bradley translation omits the first of the chapters listed above and the appendixes, since these were given in Volume 1. As with Volume 1, there is an index to the Bradley translation but not to the Boudart one.

As mentioned in the review of Volume 1, the great value of these translations is to bring more easily to workers in the West the views of the major Russian school of chemical kinetics. Volume 2 is again of great value from this point of view. It is, however, rather disappointing compared with Volume 1, and could largely have been written in 1935 at the time of Semenov's classical work on chain reactions. In particular, the chapters which deal with oxidation reactions are disappointing and give little indication that progress is at last being made on the chemistry of such processes. Nevertheless, because it helps to further contact between Russian work and that in the West, the book is a "must" for all laboratories interested in chemical kinetics.

E. W. R. STEACIE,
National Research Council
Ottawa, Canada

Ion Exchange. A Laboratory Manual

J. E. Salmon, Battersea College of Technology, and *D. K. Hale*, National Chemical Laboratory, Teddington. Butterworths Scientific Publications. Academic Press, Inc., New York, 1959. vii + 136 pp. 33 figs., 5 tables. 15 × 22 cm. $5.

This is a short practical textbook with an account of the fundamental principles of ion exchange and detailed procedures for several illustrative examples. Both theory and practice are at a level that can be understood and used by superior high school students or beginning college students. It is intended primarily as a teaching aid, and presumably covers the order of a month's work at the elementary level.

The introduction covers the history of the method, the nature of ion exchange materials, and the principal types of resins and their individual characteristics. The second chapter gives detailed directions for synthesizing several types of resins from commercially available starting materials. A far more useful feature is a detailed table of commercial resins with names, designations, properties, and manufacturers. Another useful table lists equivalent resins which may be substituted for each other.

A chapter on properties treats the swelling phenomenon, penetration, equilibria, factors which determine distribution, orders of affinity in groups of ions, and includes a simplified discussion of kinetics. Column behavior and chromatography are discussed in the next chapter, which includes "break-through," "sharpening" versus "diffusing" boundaries, frontal, displacement and elution techniques, and the theoretical plate concept. A few simple formulae are given, but no derivations.

The experimental part is preceded by some useful general techniques for setting up columns, maintaining and adjusting flow rates, fraction cutters, etc. Detailed, easy-to-follow directions are given to illustrate the theory covered: preparation of washed, air dried resin; determination of resin capacity and rate of exchange; conversion of resin from one form to another; break-through capacity of a column; regeneration of a column; determination of total salt concentration; removal of interfering ions; preparation of an acid from a salt; demineralization of water; separation of iron and copper; and the behavior of cupric and ferric complexes. Conclusions are given at the end of each experiment pointing out the implications of the results.

Literature references follow each chapter and a list of recent monographs is given at the end. In general the text is well written, accurate and free from misprints. This reviewer's criticisms are minor: directions for synthesizing resins seem out of place with the otherwise elementary scope, the terms "Type I" and "Type II" resins are used several times but never defined clearly, and on page 88 it is suggested that copper can be determined by titration with thiosulfate. In view of the otherwise very specific instructions, this latter suggestion needs amplification.

The book can be recommended as an excellent introduction to ion exchange. Its non-mathematical approach will please some and will stimulate others to pursue more advanced works.

ROBERT L. PECSOK
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Los Angeles, Calif.

Gmelins Handbuch der Anorganischen Chemie. Special Volume: Alphabetic Series to Systematic Subject Index

Edited by the Gmelin Institute. 8th ed. Verlag Chemie, GmbH, Weinheim/Bergstr., 1959. 109 pp. 17.5 × 25 cm. Paperbound, $7; cloth bound, $8.50.

The "Alphabetic Series," with bilingual test in German and English, is a supplement to the "Systematic Subject Index." The classification terms in the alphabetic series carry code numbers—which are likewise listed in the "Systematic Subject Index"—so that the location of a concept within the proper group in the system can be established. The alphabetic series contains over 50% more terms than the systematic index.

Gmelins Handbuch der Anorganischen Chemie. System 15: Silicon, Part C, Organos Silicon Compounds

Edited by the Gmelin Institute under the direction of *E. H. E. Pietsch*. 8th ed. Verlag Chemie, GmbH, Weinheim/Bergstr., 1959. xii + 501 pp. 41 figs. 156 tables. 17.5 × 25 cm. $67.44.

The Gmelin Silicon C volume deals with the chemistry of the non-mineral compounds of silicon, sometimes called the organosilicon compounds. The surge of new literature concerning these compounds has been prompted by the increase in industrial applications for silicones.

The preparation and properties of silicon-hydrogen compounds forms the main portion of the Silicon C volume. These compounds are arranged according to the following groups: Tetraalkyl-, alkylhydrogen-, halogeno-, thio-, amino-, and alkoxy-silanes, silanoles, siloxanes, and silicic acid esters. More than 3000 compounds are either separately described or their characteristics summarized by groups in table form.

An added feature of this volume is the presentation of special manufacturing problems and of the chemical and physical properties which are important for industrial use of silicones. Applications for silicones in oils, pastes, greases, resins, and rubbers are discussed.

Although all German headings and subheadings are accompanied by English translations, no English subject index is included.

THEODORE R. WILLIAMS
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Gmelins Handbuch der Anorganischen Chemie. System 5. Fluorine Supplement

Edited by the Gmelin Institute under the direction of *E. H. E. Pietsch*. 8th ed. Verlag Chemie, GmbH, Weinheim/Bergstr., 1959. xviii + 258 pp. 31 figs. 17.5 × 25 cm. $36.

The increase in the new knowledge of fluorine chemistry during the years 1936 to 1949 is evidenced by the size of the supplement to the fluorine volume. The main volume comprised only 86 pages as compared with the 258 pages in the addendum. This volume deals with the compounds that fluorine forms with nitrogen, hydrogen, and oxygen.

The chapter devoted to the occurrence of fluorine contains a detailed review of the numerous fluorine content determinations of minerals, water, and biological substances. Dental applications of fluorine chemistry have led to extensive investigations in this field.

A chapter is devoted to the manufacture of fluorine by electrolytic means. Details of the most important method of preparation of hydrofluoric acid by the decomposition of fluorite are given. The laboratory preparations of fluorine compounds are discussed. A chapter on Toxicity deals with the hazards in handling fluorine and fluorine compounds, and safety requirements.

The physical properties of fluorine, hydrofluoric acid, and other compounds are thoroughly reviewed.

The use of anhydrous HF as a solvent and its reaction with organic compounds is described and detailed accounts of the chemical reactions of fluorine and hydrofluoric acid are given.

Special analytical methods are presented in the chapter dealing with detection and determination. The compounds of fluorine with nitrogen, hydrogen, and oxygen are thoroughly reviewed.

The innovation of a German-English table of contents enhances the accessibility of the information contained in the volume.

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Theoretical Organic Chemistry

Proceedings and Discussions of the Kekulé Symposium, London, September 15–17, 1958. IUPAC. Butterworths Publications, Ltd., London, 1959. Sole USA distributors, Academic Press Inc., New York. xvii + 298 pp. Figs. and tables. 15 × 22 cm. $9.50.

This volume represents the full proceedings of the Kekulé Symposium on Theoretical Organic Chemistry held in London in September, 1958, under the auspices of The Chemical Society and the IUPAC. The 19 papers are concerned with structure and chemical bonding, and electrophilic, nucleophilic, and homolytic reactions. These papers provide an excellent review of modern ideas in aromatic

(*Continued on page A174*)